Manganese-Catalyzed Selective Oxidation of Aliphatic C-H groups and Secondary Alcohols to Ketones with Hydrogen Peroxide

Dong, Jia Jia; Unjaroen, Duenpen; Mecozzi, Francesco; Harvey, Emma C.; Saisaha, Pattama; Pijper, Dirk; de Boer, Johannes W.; Alsters, Paul; Feringa, Ben L.; Browne, Wesley R.

Published in:
Chemsuschem

DOI:
10.1002/cssc.201300378

Publication date:
2013

CHEMISTRY & SUSTAINABILITY
CHEMSUSCHEM
ENERGY & MATERIALS

Supporting Information

Manganese-Catalyzed Selective Oxidation of Aliphatic C–H groups and Secondary Alcohols to Ketones with Hydrogen Peroxide

Jia Jia Dong,[a] Duenpen Unjaroen,[a] Francesco Mecozzi,[a] Emma C. Harvey,[a] Pattama Saisaha,[a] Dirk Pijper,[a] Johannes W. de Boer,[b] Paul Alsters,[c] Ben L. Feringa,[a] and Wesley R. Browne*[a]

cssc_201300378_sm_miscellaneous_information.pdf

Table of Contents

Caution. The drying or concentration of solutions that potentially contain H_2O_2 should be avoided. Prior to drying or concentrating, the presence of H_2O_2 should be tested for using peroxide test strips followed by neutralisation on $NaHSO_3$ or another suitable reducing agent. When working with H_2O_2, suitable protective safeguards should be in place at all times.

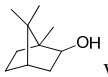
Caution. Butanedione has been linked with lung disease upon exposure to vapours. It should be handled in a properly ventilated fumehood and exposure to vapours should be avoided.

Note. **All reagents are of commercial grade and used as received unless stated otherwise.**

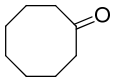
1. General Procedures and methods

Chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm, with visualization by UV, cerium/molybdenum or potassium permanganate staining. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) in CD_3CN or $CDCl_3$. Chemical shift values are reported in ppm with the resonance solvent signal as the internal reference ($CHCl_3$: 7.26 for ^{1}H, 77.0 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, br = broad, m = multiplet), coupling constants (Hz), and relative integration. ^{13}C spectra were assigned based on APT ^{13}C-NMR spectroscopy.

2. Examples of reactions at > 1g scale

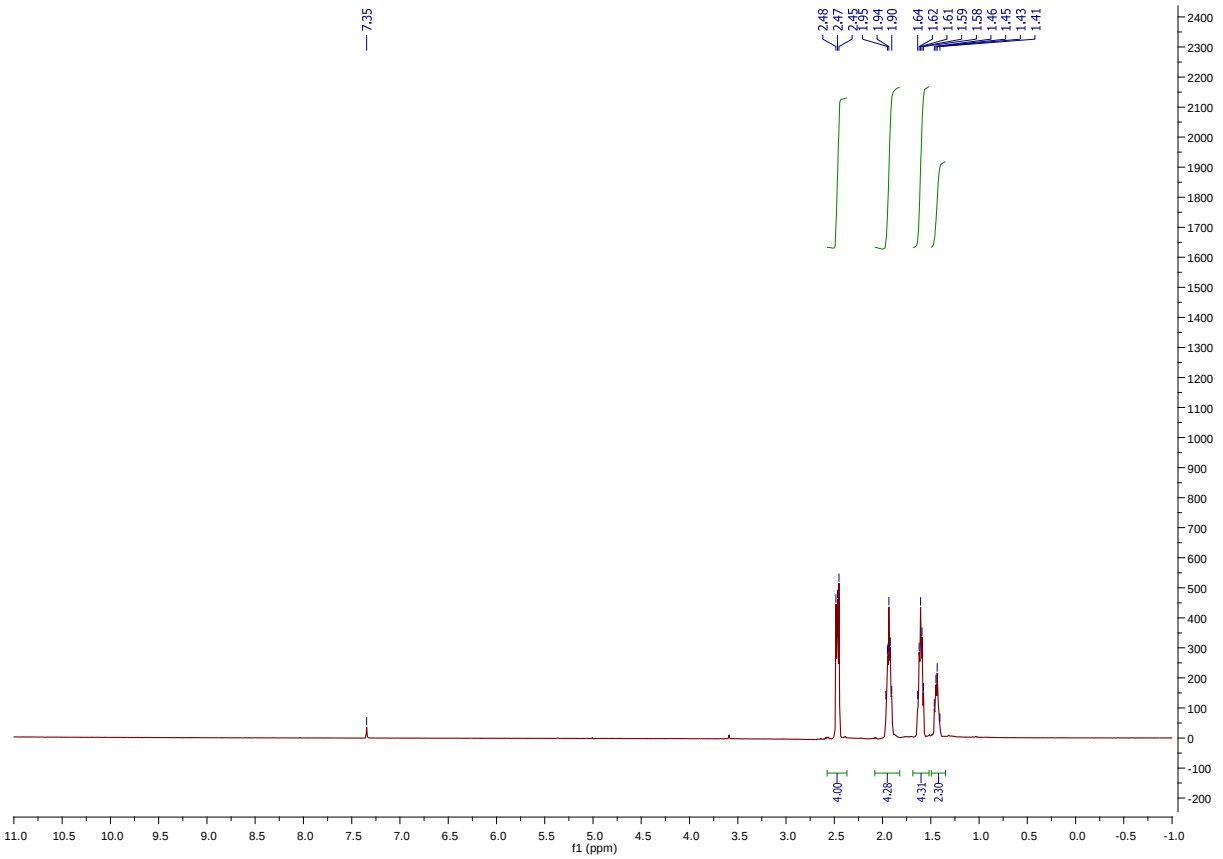
Isoborneol (4 g)  was added to a solution of $Mn^{II}(ClO_4)_2.6H_2O$ (0.01 mol %), pyridine-2-carboxylic acid (0.5 mol %), NaOAc (aq. 0.6 M, 1 mol %) and butanedione (0.5 equiv.) in acetonitrile to give a final substrate concentration of 0.5 M. The solution was cooled in an ice/water bath before addition of H_2O_2 (50 wt. %, 3.0 equiv.) and the temperature was allowed to rise overnight with stirring. Brine was added to the reaction mixture and the product and any unreacted isoborneol extracted with dichloromethane (3 by 10 mL). The combined organic layers were reduced *in vacuo*, with residual dichloromethane stripped *in vacuo* by addition of acetonitrile. Isoborneol was converted (63%) with full selectivity towards camphor  . The crude mixture was subjected to the same reaction conditions resulting in full conversion of the isoborneol. Camphor was isolated in 87 % yield (3.45 g) after purification by flash column chromatography on silica gel (pentane/ether = 9/1, Rf = 0.3). The product was characterised by ^{1}H NMR spectroscopy (vide infra).

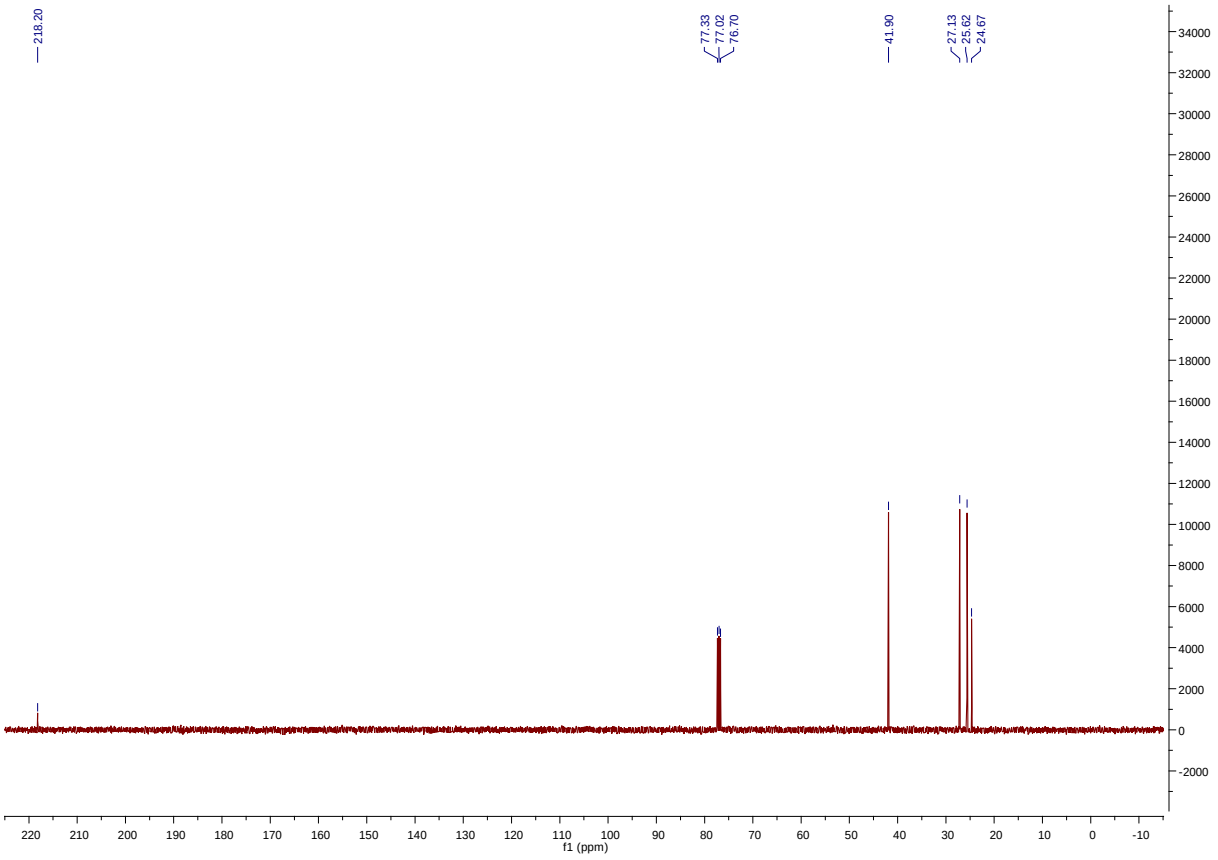
3. Characterization of isolated products

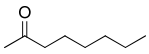


Cyclooctanone (Table 1, entry 2) Isolated by flash column chromatography on silica gel (dichloromethane/ether = 9:1, Rf = 0.5).The title compound was obtained as a colorless oil (78% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (m, 4H), 1.94 (m, 4H), 1.62 (m, 4H), 1.43(m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.2, 41.9, 27.1, 25.6, 24.7.

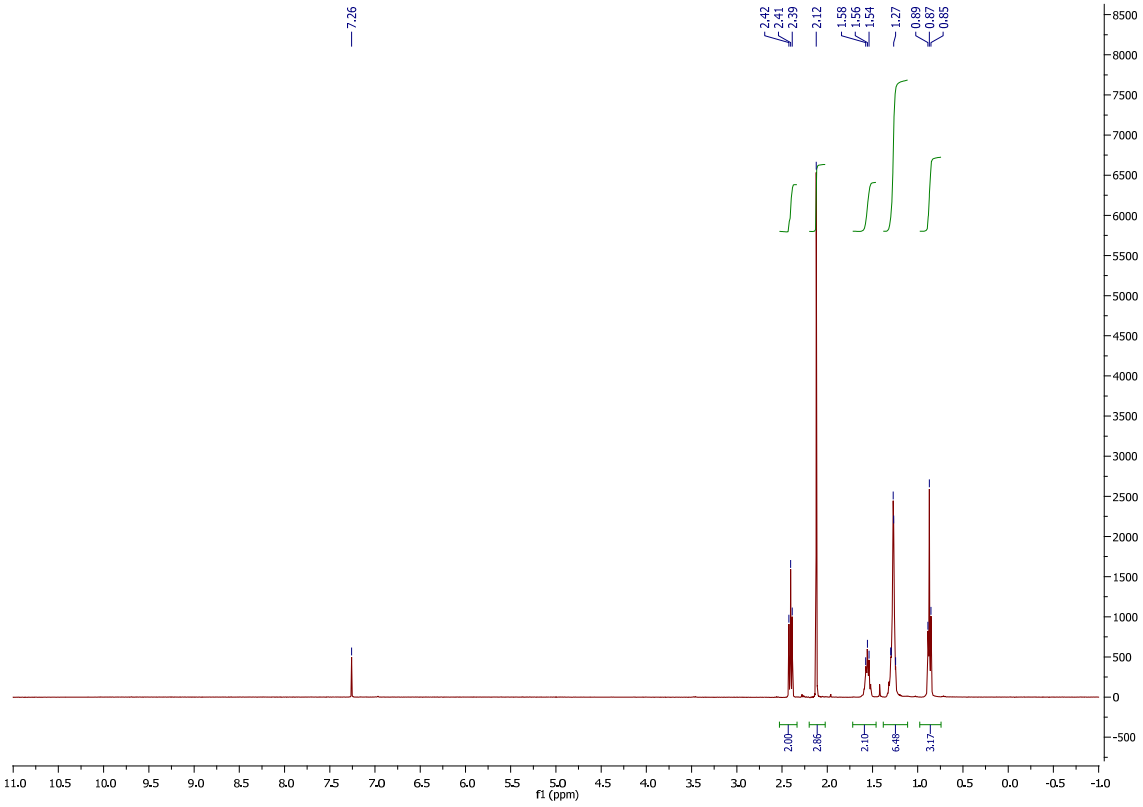


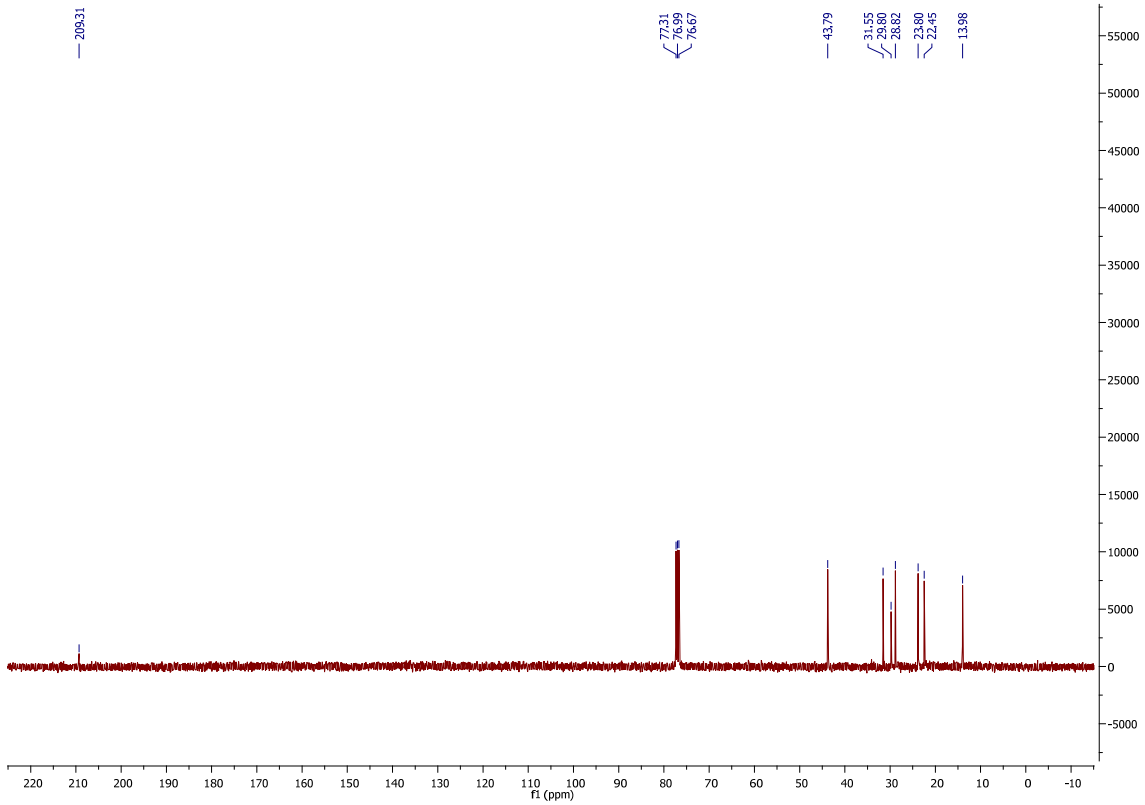

218.20
77.33
77.02
76.70
41.90
27.13
25.62
24.67
f1 (ppm)

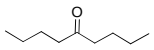


2-Octanone (Table 1, entry 3) Isolated by flash column chromatography on silica gel (pentane/ether = 9:1, Rf = 0.5). The title compound was obtained as a colorless oil (88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (t, *J* = 7.4 Hz, 2H), 2.12 (s, 3H), 1.56 (m, 2H), 1.27(br, 6H, CH_2), 0.88 (t, *J* = 7.3 Hz, 3H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3, 43.8, 31.6, 29.8, 28.8, 23.8, 22.4, 14.0.

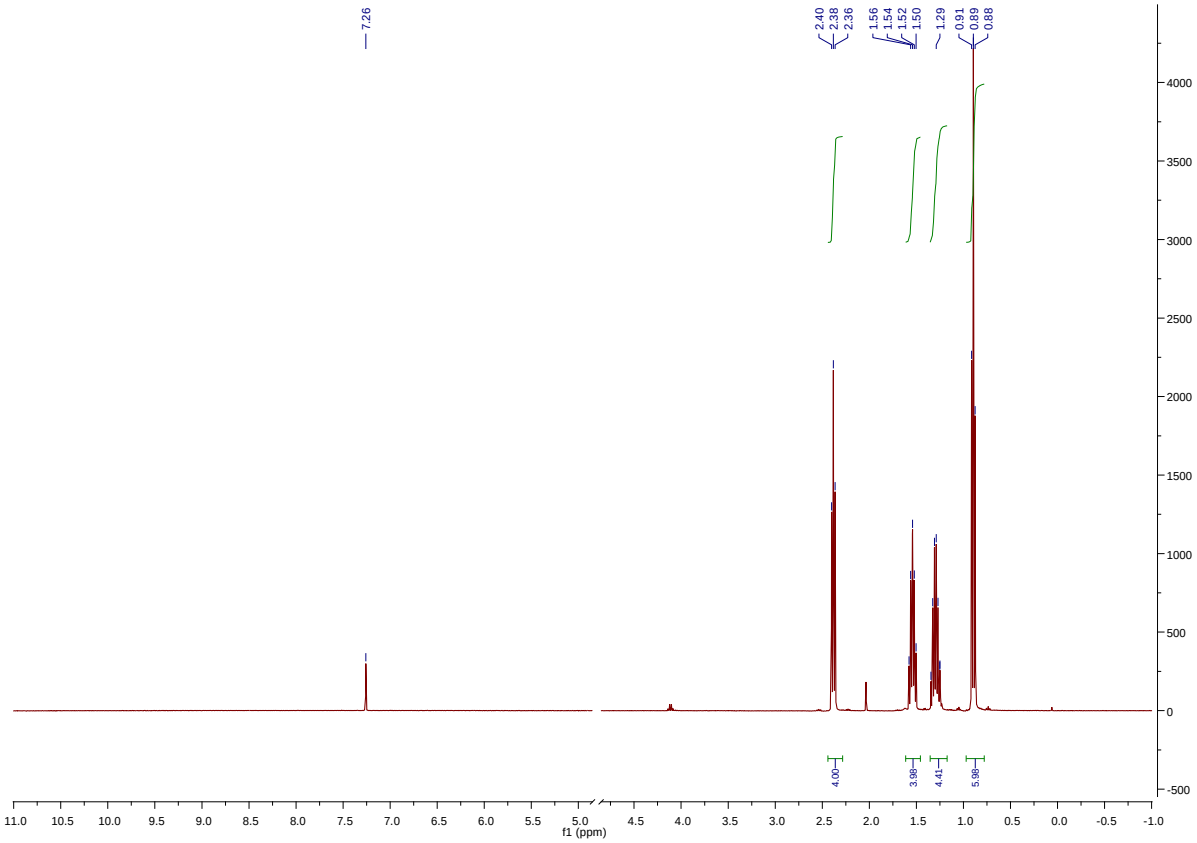


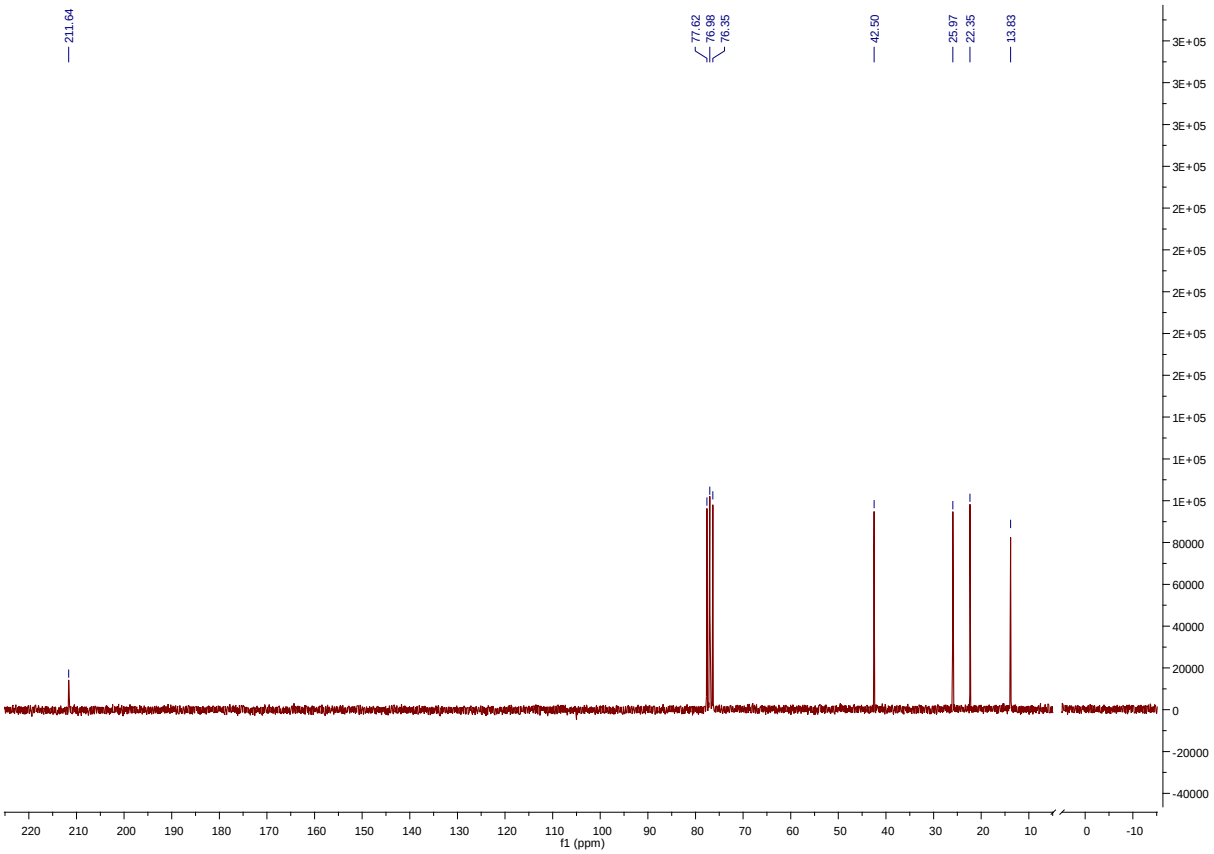

209.31
77.31
76.99
76.67
43.79
31.55
29.80
28.82
23.80
22.45
13.98
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



Nonan-5-one (Table 1, entry 4) Isolated by flash column chromatography on silica gel (pentane/ether = 95/5, Rf = 0.5).The title compound was obtained as a colorless oil (72% yield).

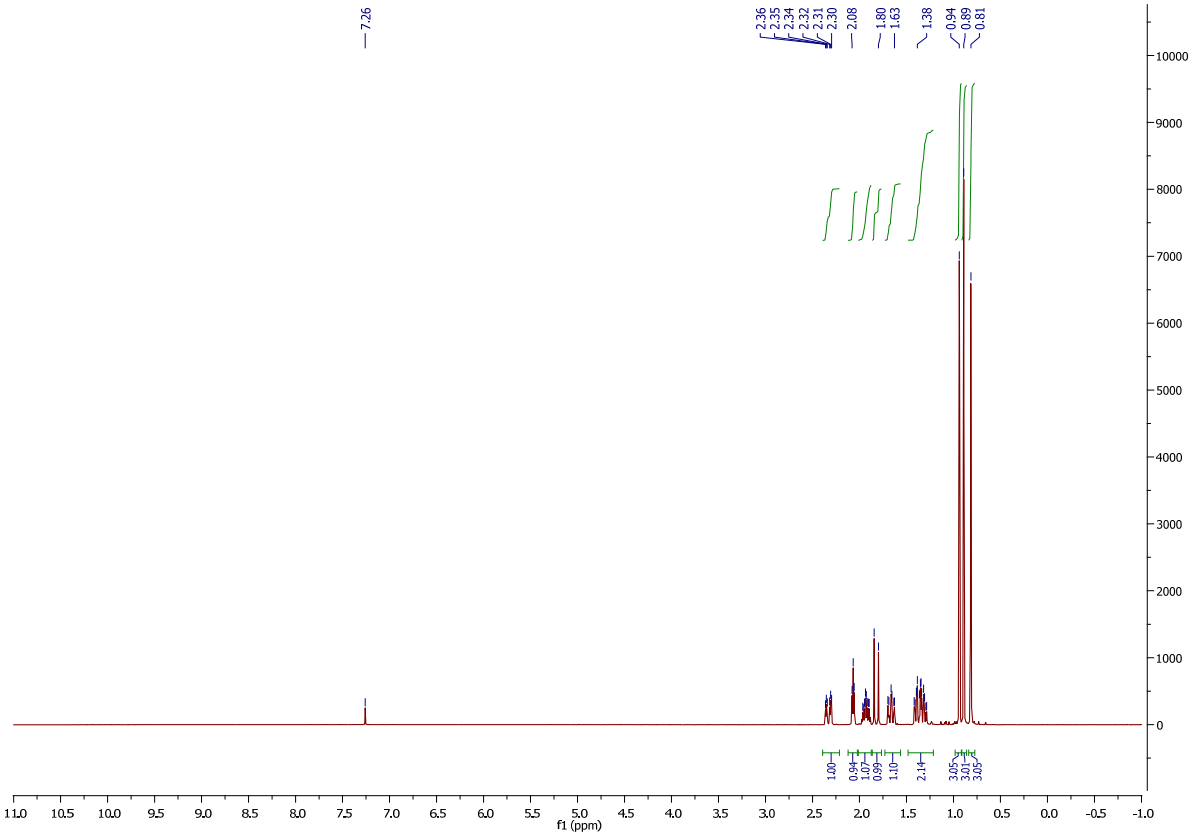
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40-2.36 (t, *J* = 7.4 Hz, 4H), 1.58-1.50 (q, *J* = 7.4 Hz, 4H), 1.35-1.25 (sextuplet, *J* = 7.4 Hz, 4H), 0.91-0.88 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.6, 42.5, 26.0, 22.3, 13.8.

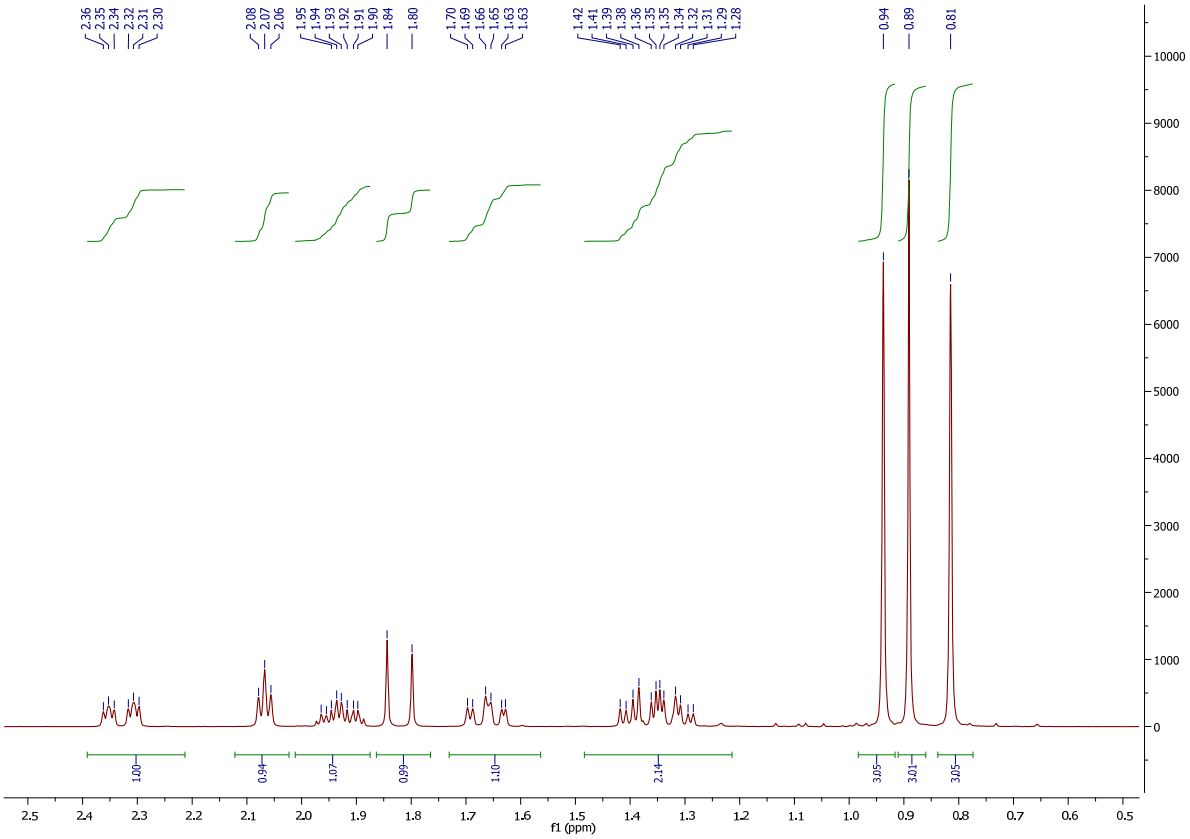


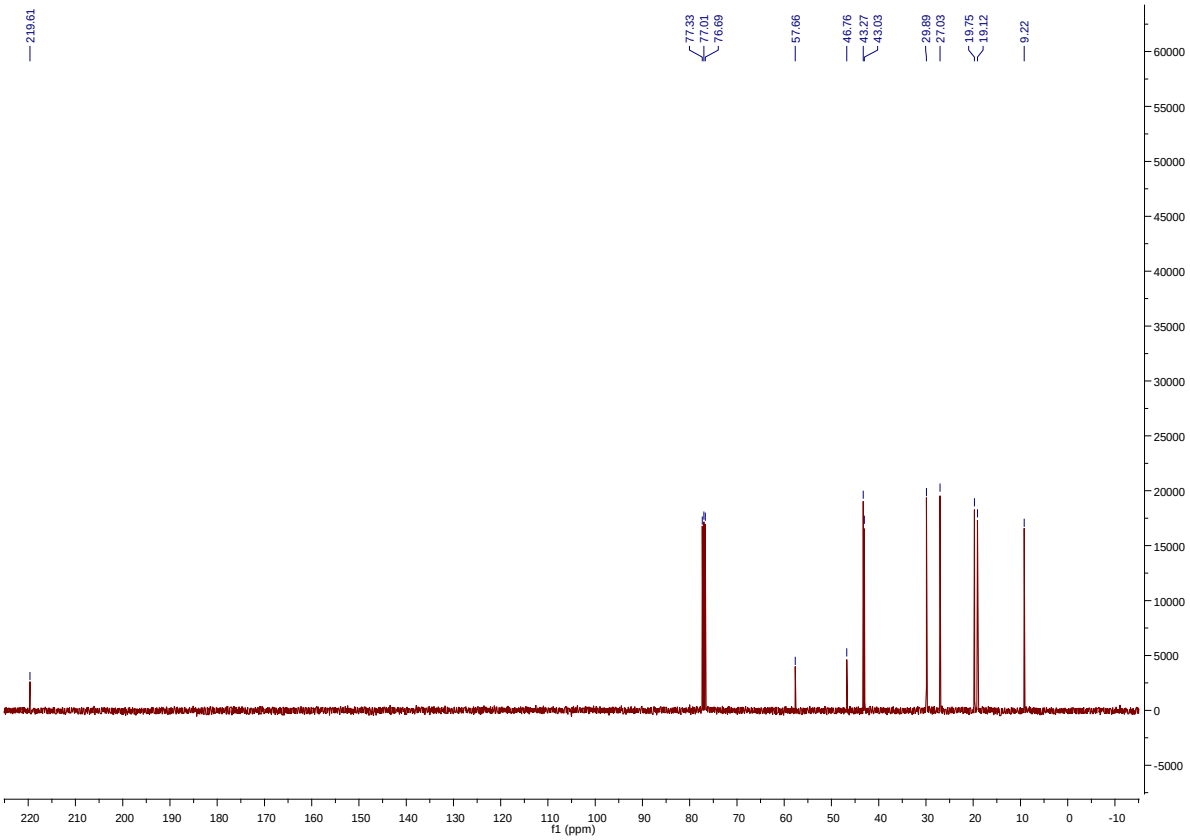

211.64
77.62
76.98
76.35
42.50
25.97
22.35
13.83
3E+05
2E+05
1E+05
80000
60000
40000
20000
0
-20000
-40000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Camphor (Table 1, entry 6) Isolated by flash column chromatography on silica gel (pentane/ether = 9/1, Rf = 0.3).The title compound was obtained as a white solid (95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36-2.30 (m, 1H), 2.08 (t, *J* = 4.5, 1H), 1.96-1.90 (m, 1H), 1.83 (d, *J* = 18.2, 1H), 1.70-1.63 (m, 1H), 1.42-1.28 (m, 2H), 0.94(s, 3H), 0.89 (s, 3H), 0.81(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 219.6, 57.7, 46.8, 43.2, 43.0, 29.9, 27.0, 19.8, 19.1, 9.2.

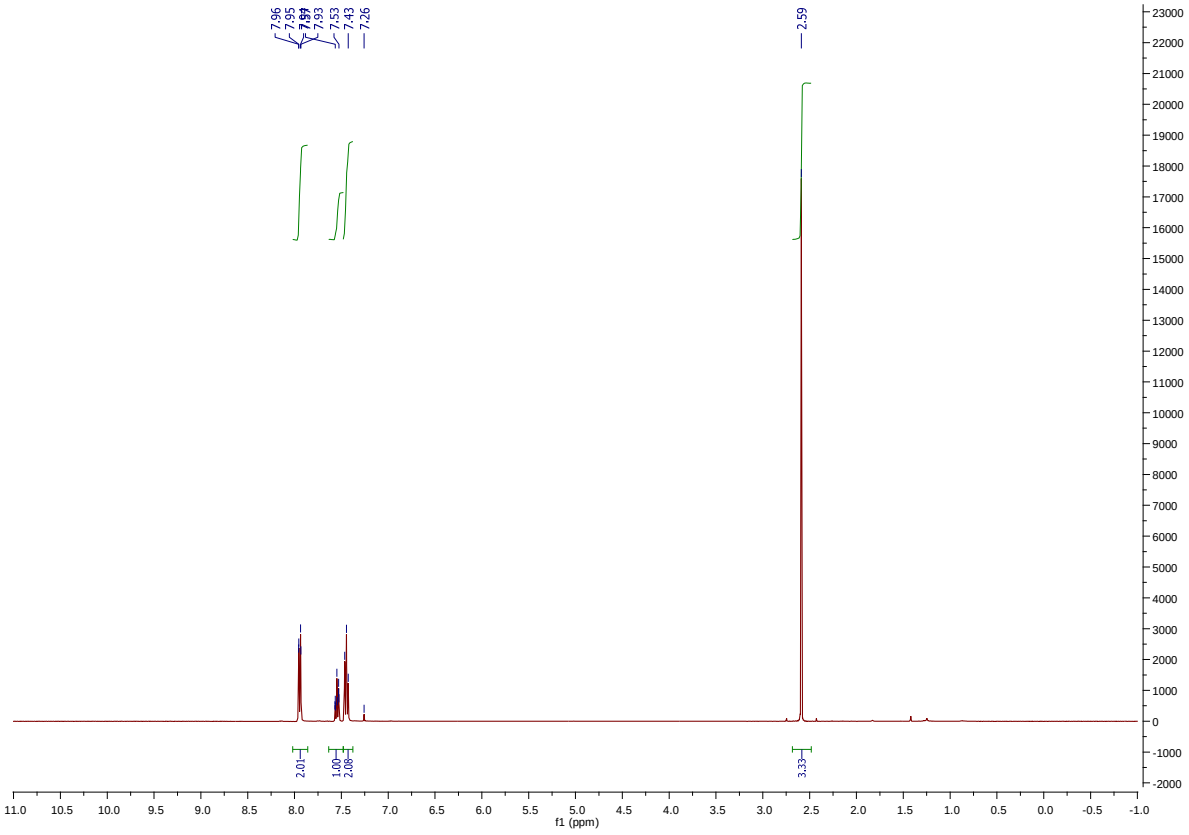


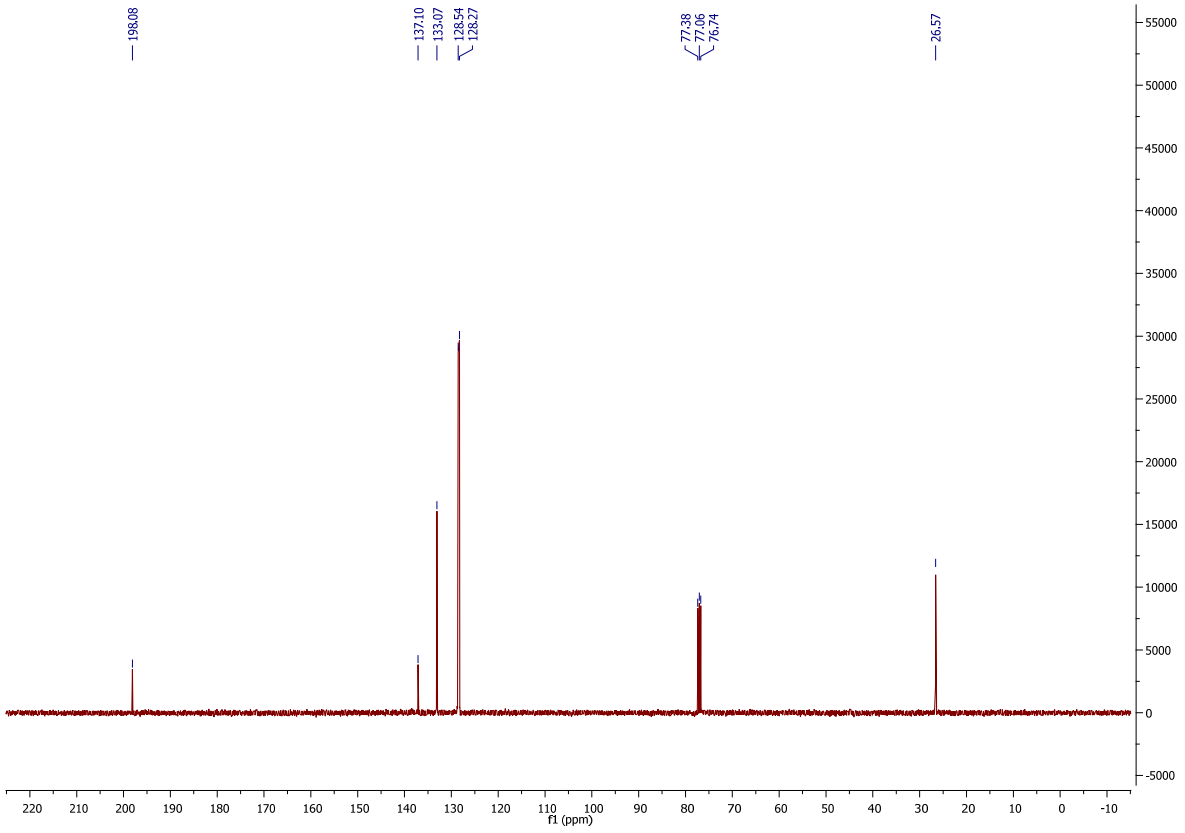

2.36
2.35
2.34
2.32
2.31
2.30
2.08
2.07
2.06
1.95
1.94
1.93
1.92
1.91
1.90
1.84
1.80
1.70
1.69
1.66
1.65
1.63
1.63
1.42
1.41
1.39
1.38
1.36
1.35
1.35
1.34
1.32
1.31
1.29
1.28
0.94
0.89
0.81
1.00
0.94
1.07
0.99
1.10
2.14
3.05
3.01
3.05
f1 (ppm)

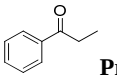

219.61
77.33
77.01
76.69
57.66
46.76
43.27
43.03
29.89
27.03
19.75
19.12
9.22
f1 (ppm)

Acetophenone (Table 1, entry 7) Isolated by flash column chromatography on silica gel (pentane/ether = 9/1, Rf = 0.3).The title compound was obtained as a colorless oil (90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.03 (m, 2H), 7.57-7.53 (m, 1H), 7.46-7.43 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 137.1, 133.1, 128.5, 128.3, 26.6.

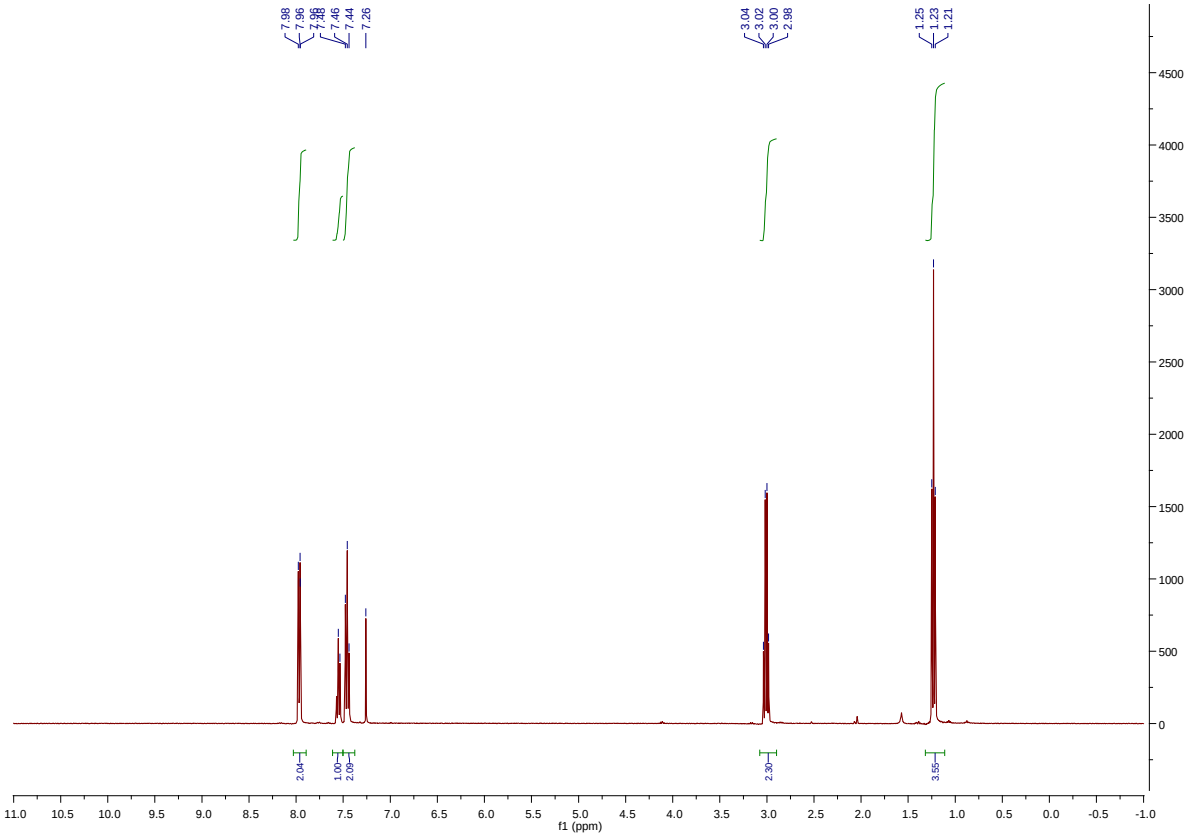


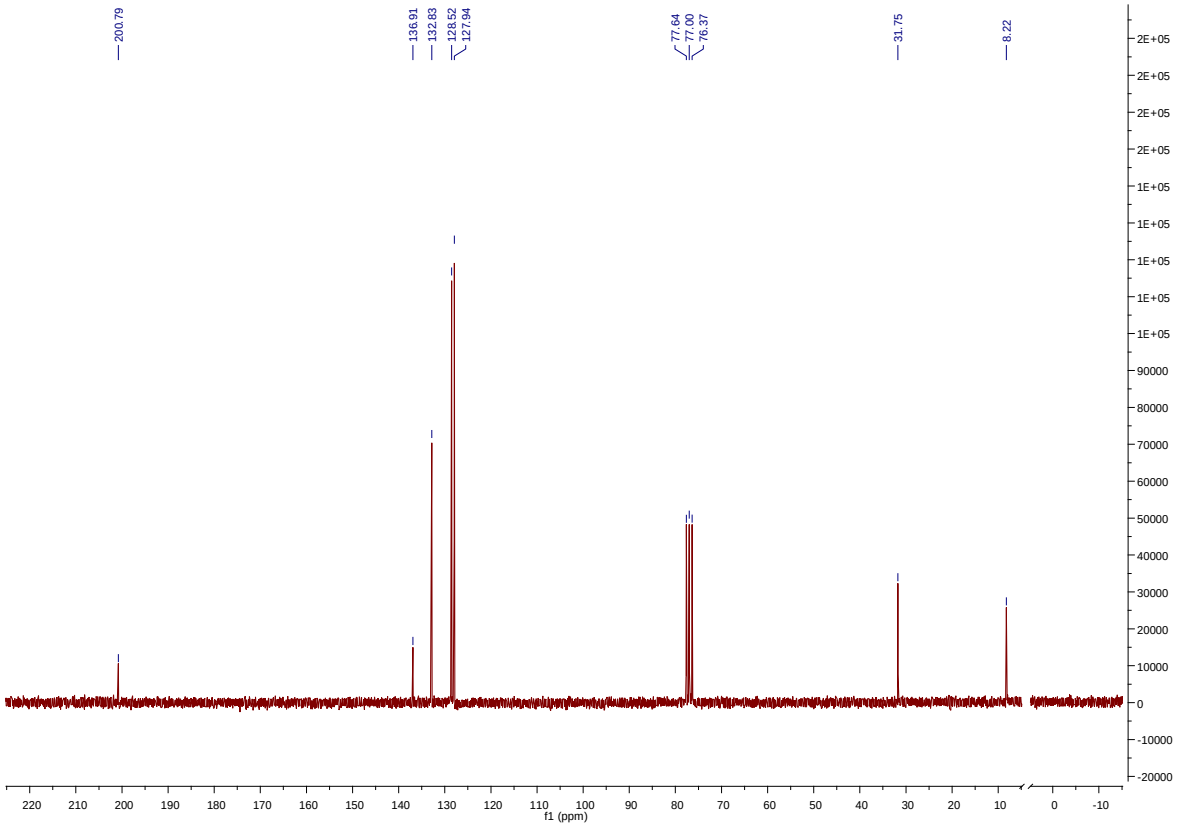

198.08
137.10
133.07
128.54
128.27
77.38
77.06
76.74
26.57
f1 (ppm)

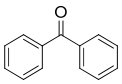


Propiophenone (Table 1, entry 8) Isolated by flash column chromatography on silica gel (pentane/ethyl acetate = 95/5, Rf = 0.5).The title compound was obtained as a colorless oil (77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.98-7.96 (m, 2H), 7.57-7.53 (m, 1H), 7.48-7.44 (m, 2H), 3.04-2.98 (q, *J* = 7.2 Hz , 2H), 1.25-1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 136.9, 132.8, 128.5, 127.9, 31.8, 8.2.

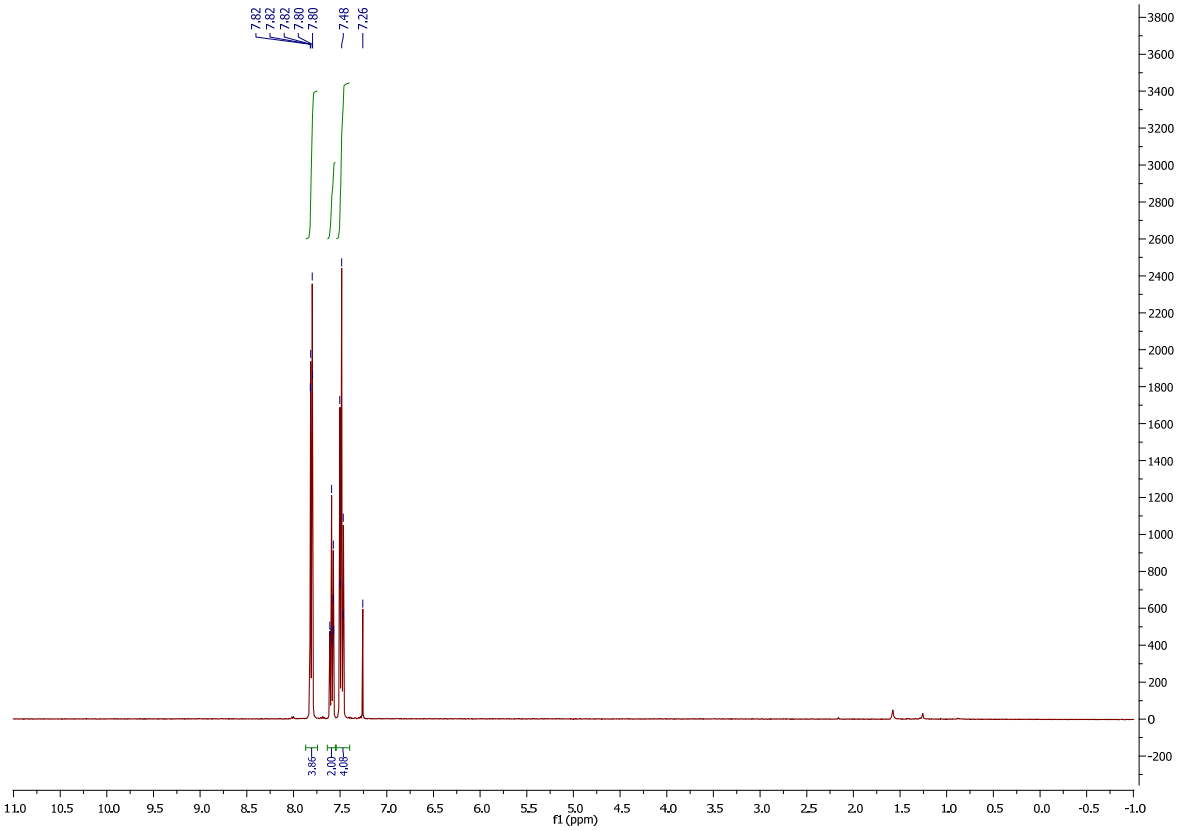


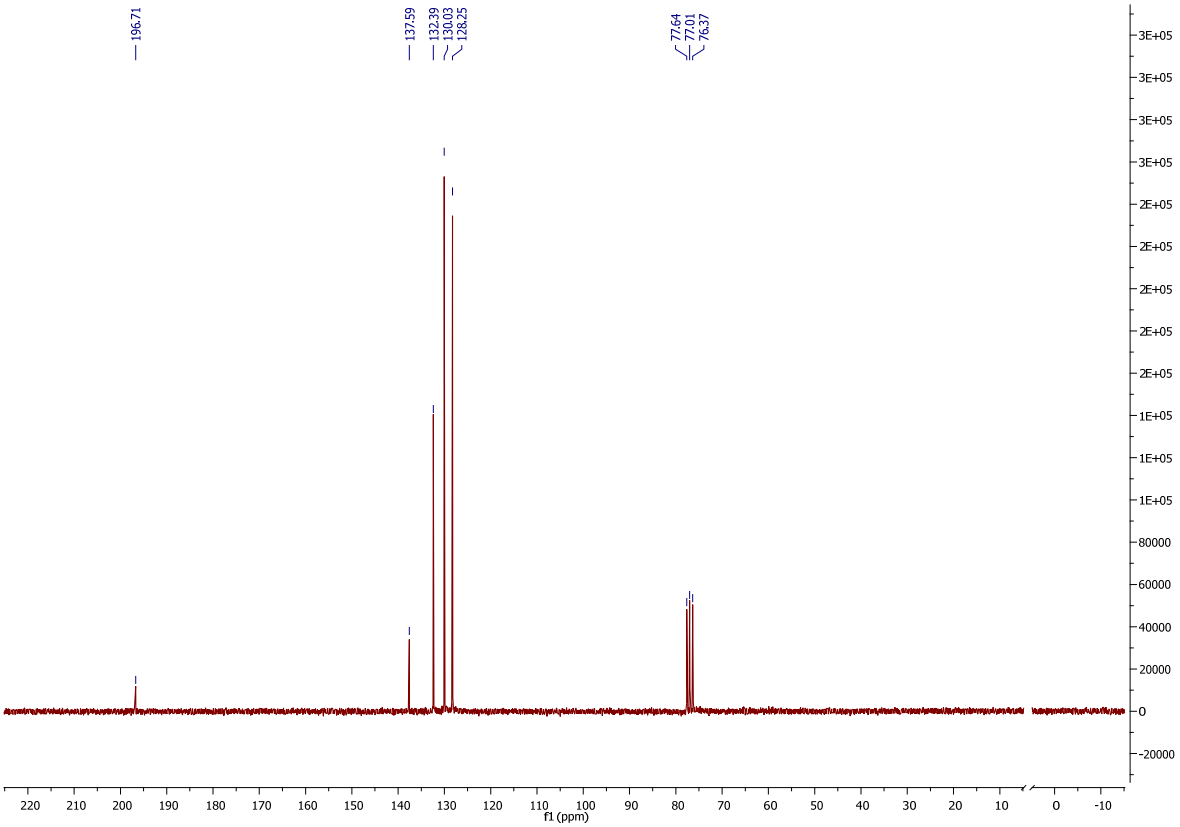

200.79
136.91
132.83
128.52
127.94
77.64
77.00
76.37
31.75
8.22
f1 (ppm)



Benzophenone (Table 1, entry 9) Isolated by flash column chromatography on silica gel (pentane/ethyl acetate = 95/5, Rf = 0.5).The title compound was obtained as a colorless oil (80% yield).

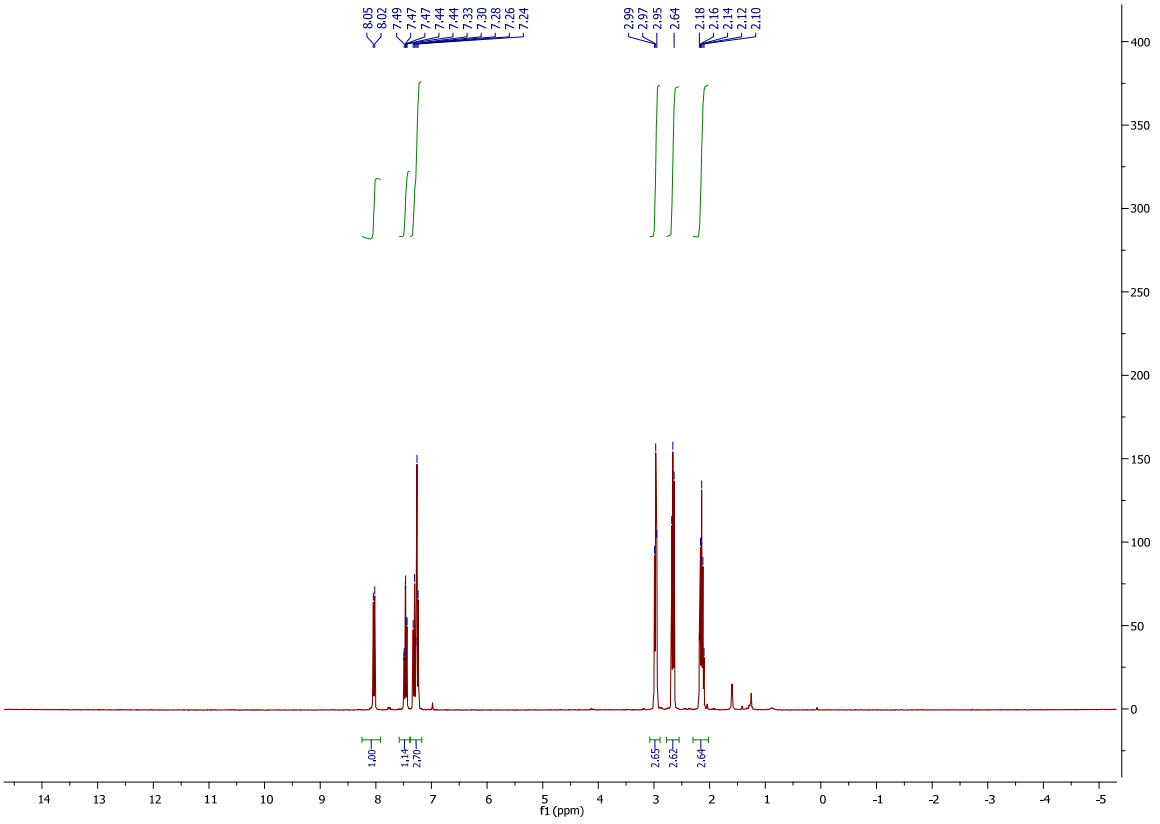
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.80 (m, 4H), 7.61-7.57 (m, 2H), 7.50-7.47 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 137.6, 132.4, 130.0, 128.3.

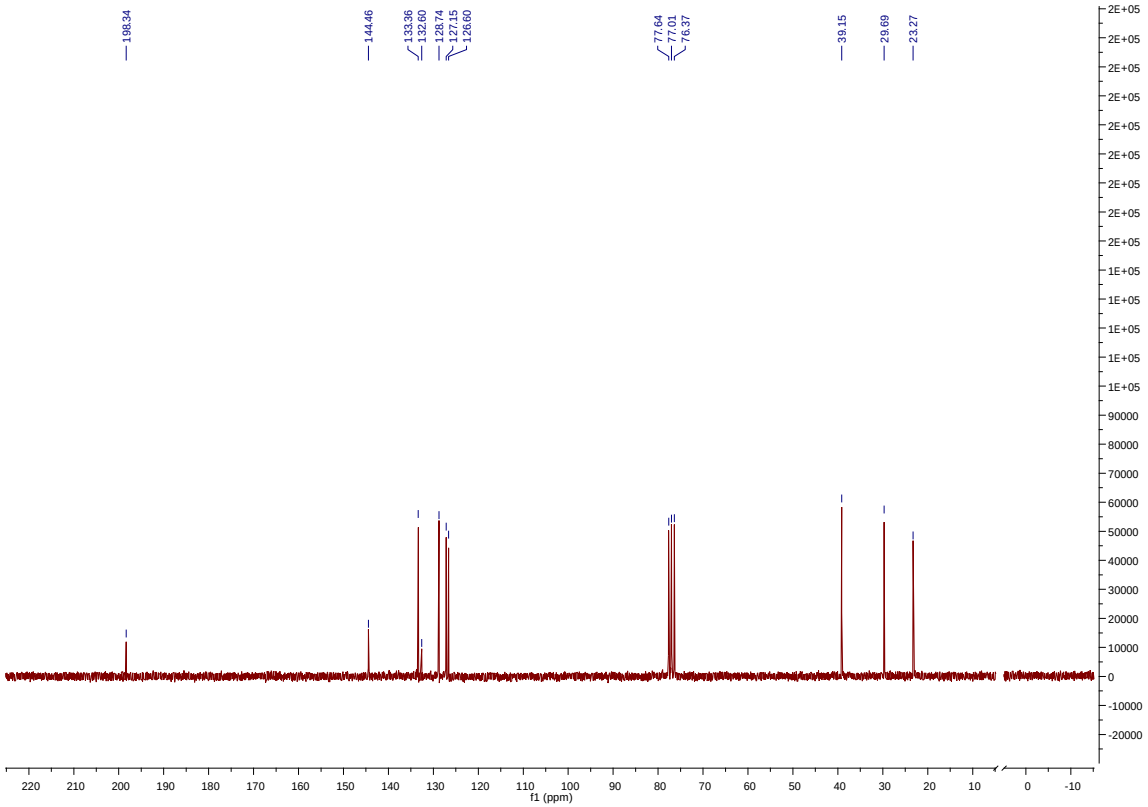


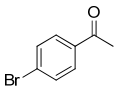

196.71
137.59
132.39
130.03
128.25
77.64
77.01
76.37
f1 (ppm)

3,4-dihydronaphthalen-1(2H)-one (Table 1, entry 10) Isolated by flash column chromatography on silica gel (pentane/ethyl acetate = 95/5, Rf = 0.5).The title compound was obtained as a yellowish oil (75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.02 (m, 1H), 7.49-7.44 (m, 1H), 7.33-7.24 (m, 2H), 2.99-2.95 (t, *J* = 6.1 Hz, 2H), 2.68-2.64 (dd, *J* = 6.2 Hz, *J* = 6.8 Hz, 2H), 2.18-2.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 144.4, 133.4, 132.6, 128.7, 127.2, 126.6, 39.2, 29.7, 23.3.

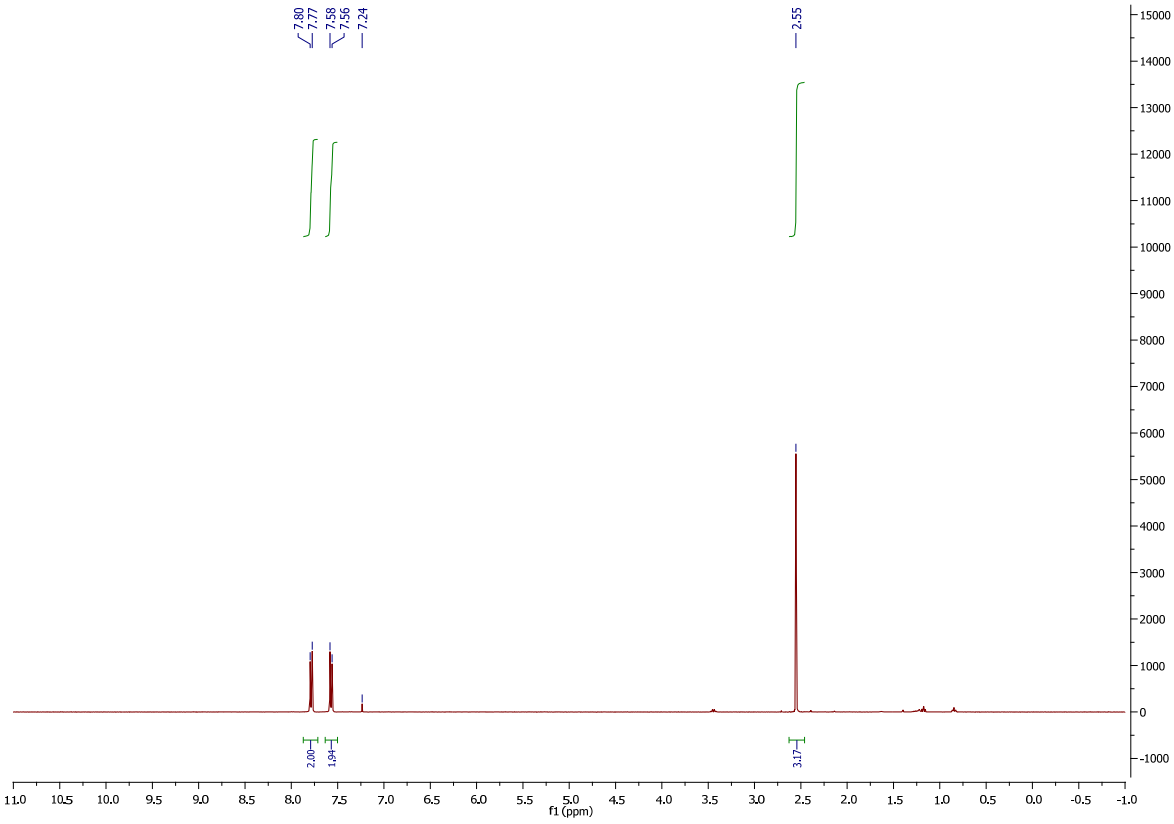


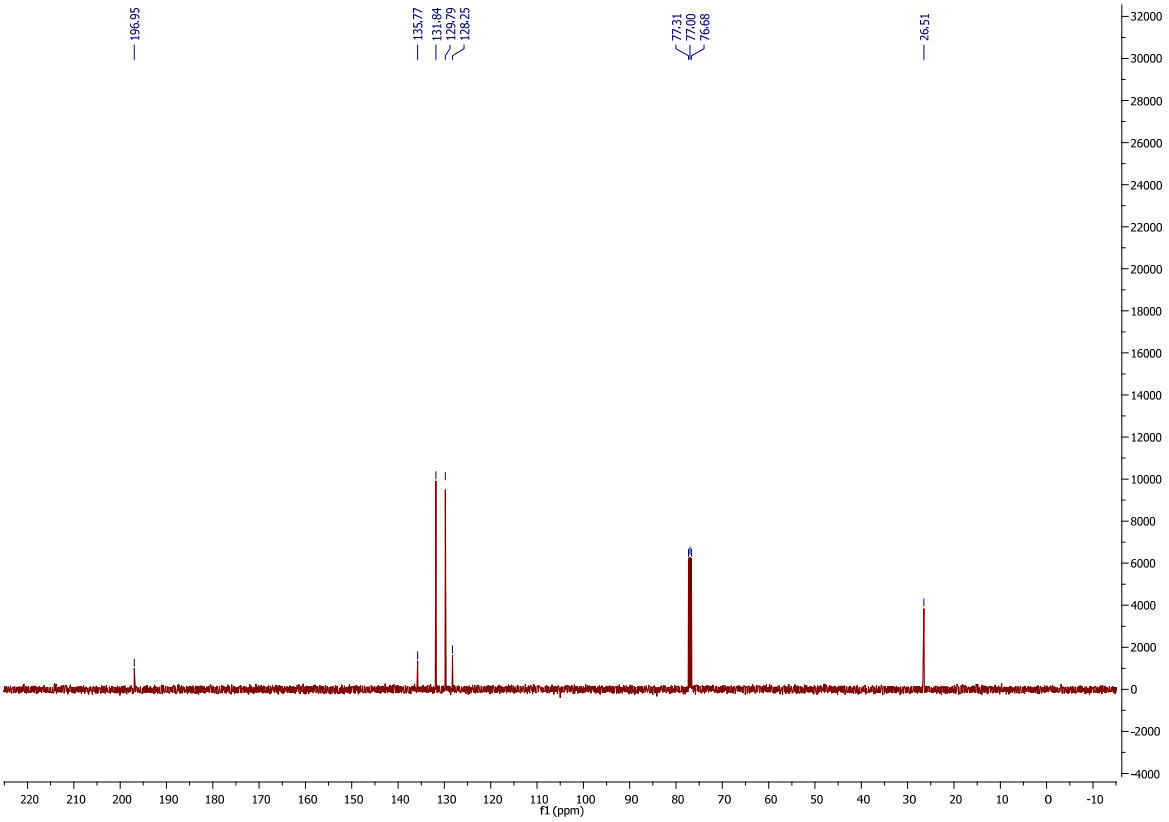

198.34
144.46
133.36
132.60
128.74
127.15
126.60
77.64
77.01
76.37
39.15
29.69
23.27
f1 (ppm)

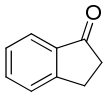


1-(4-Bromophenyl)ethanone (Table 1, entry 12) (missing) Isolated by flash column chromatography on silica gel (pentane/ether = 9/1, Rf = 0.5).The title compound was obtained as white solid (76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.77 (d, *J* = 8.6 Hz, 2H), 7.58-7.56 (d, *J* = 8.6 Hz, 2H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ197.0, 135.8, 131.8, 129.8, 128.2, 26.5.

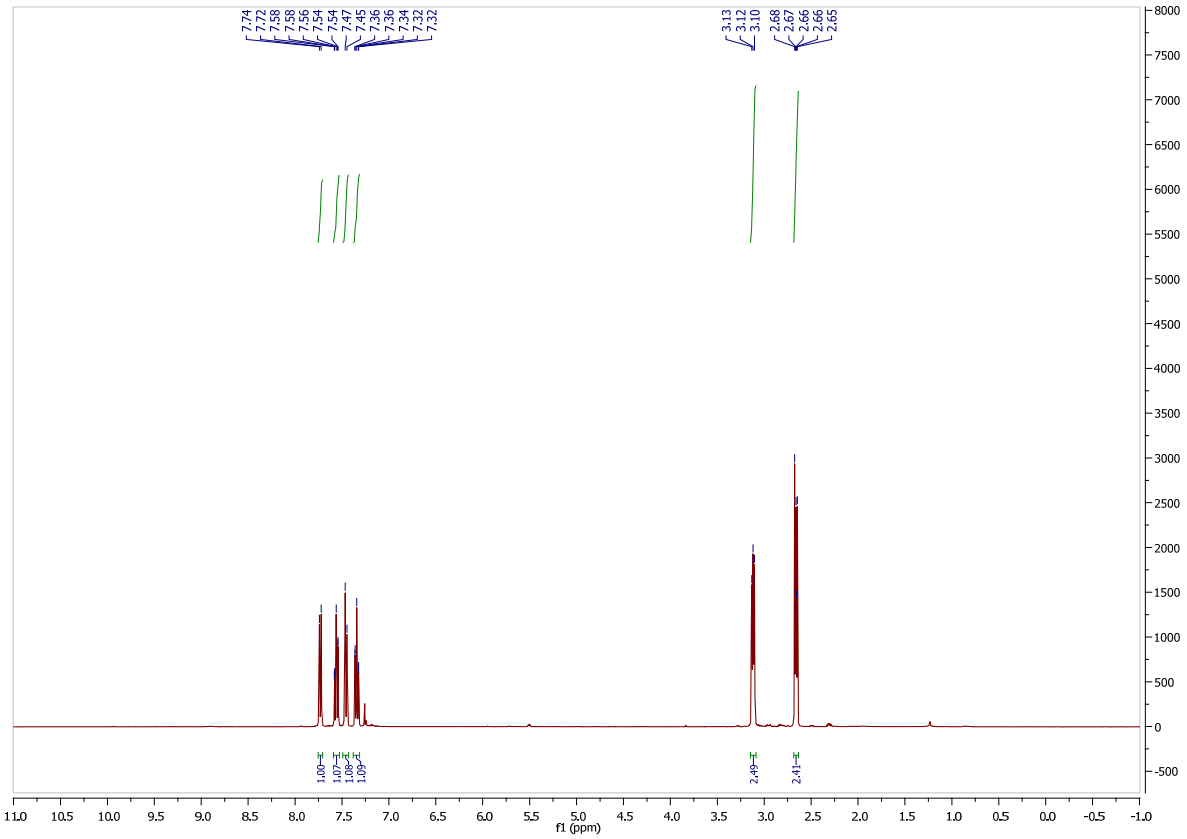


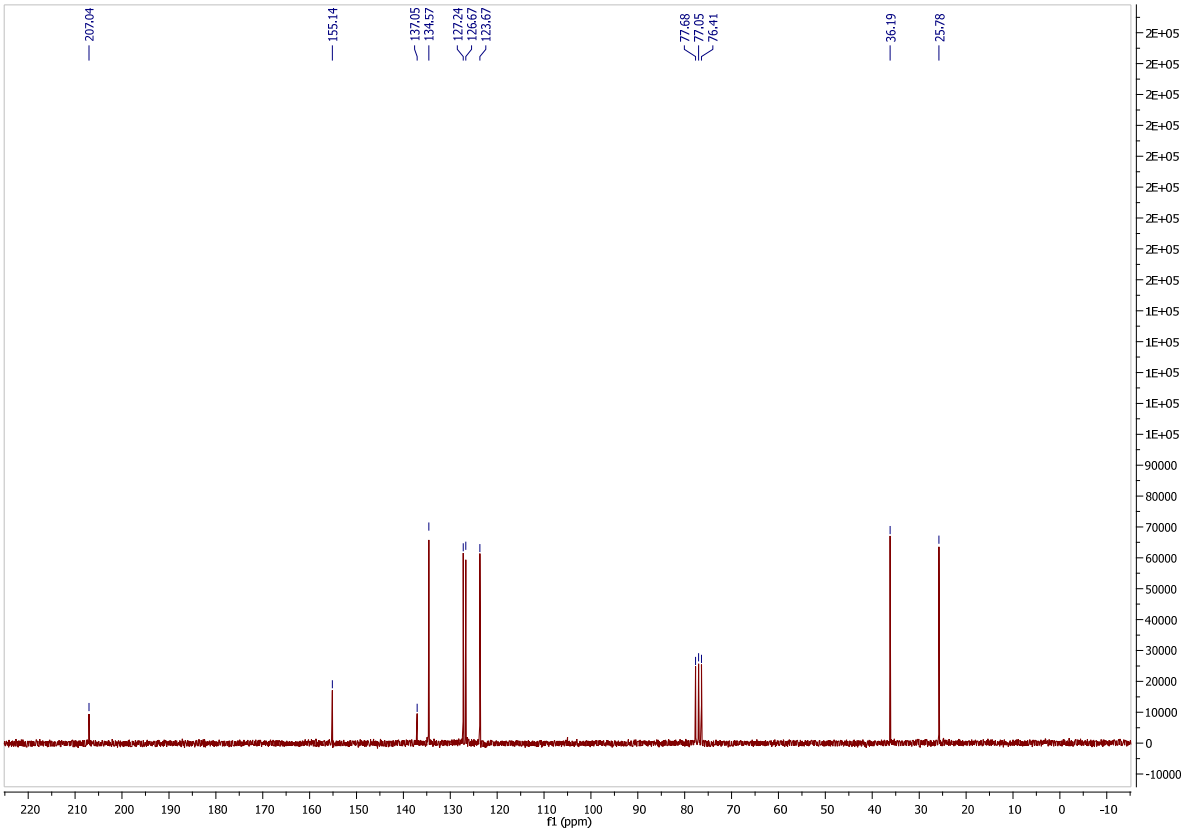

196.95
135.77
131.84
129.79
128.25
77.31
77.00
76.68
26.51
f1 (ppm)

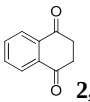


2,3-dihydro-1H-inden-1-one (Table 2, entry 5) Isolated by flash column chromatography on silica gel (pentane/ether = 80/20), Rf = 0.5).The title compound was obtained as a yellow oil (60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.14 (m, 1H), 7.60-7.56 (m, 1H), 7.48-7.46 (m, 1H), 7.38-7.34 (m, 1H), 3.13-3.10 (dd, *J* = 5.6 Hz, *J* = 6.1 Hz, 2H)), 2.68-2.65 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.0, 155.1, 137.1, 134.6, 127.2, 126.7, 123.7, 36.2, 25.8.

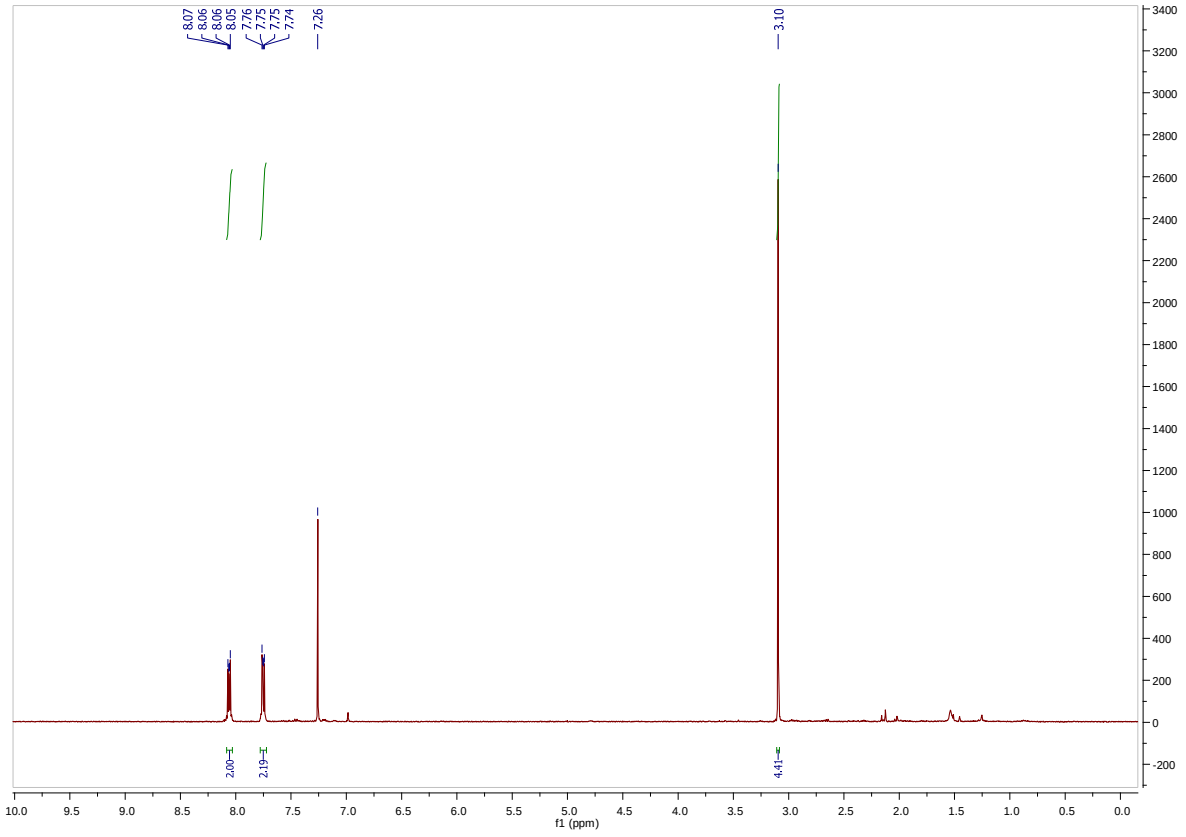


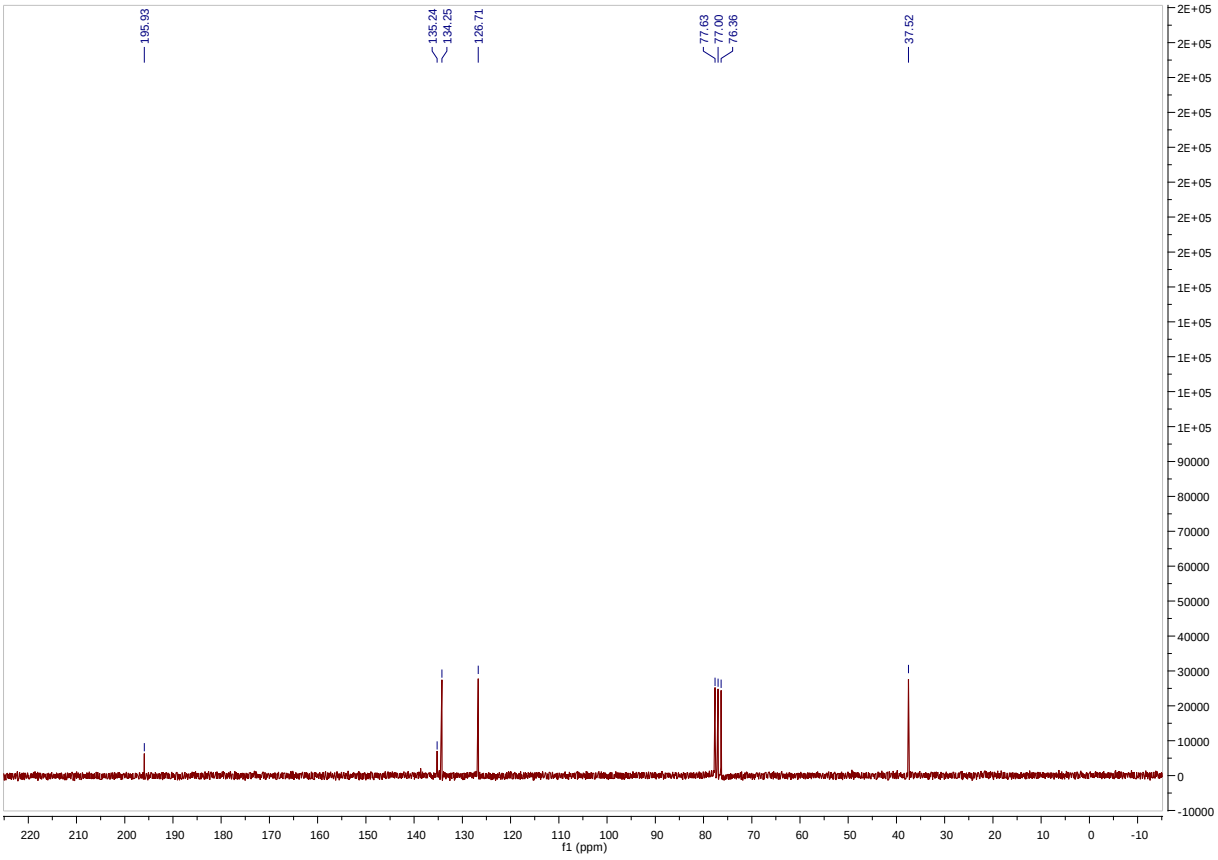

207.04
155.14
137.05
134.57
127.24
126.67
123.67
77.68
77.05
76.41
36.19
25.78
f1 (ppm)

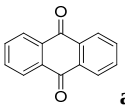


2,3-dihydronaphthalene-1,4-dione (Table 2, entry 6) Isolated by flash column chromatography on silica gel (pentane/ether = 80/20), Rf = 0.5).The title compound was obtained as a yellow oil (25% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 2H), 7.76-7.74 (m, 2H), 3.10 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 135.2, 134.3, 126.7, 37.5.

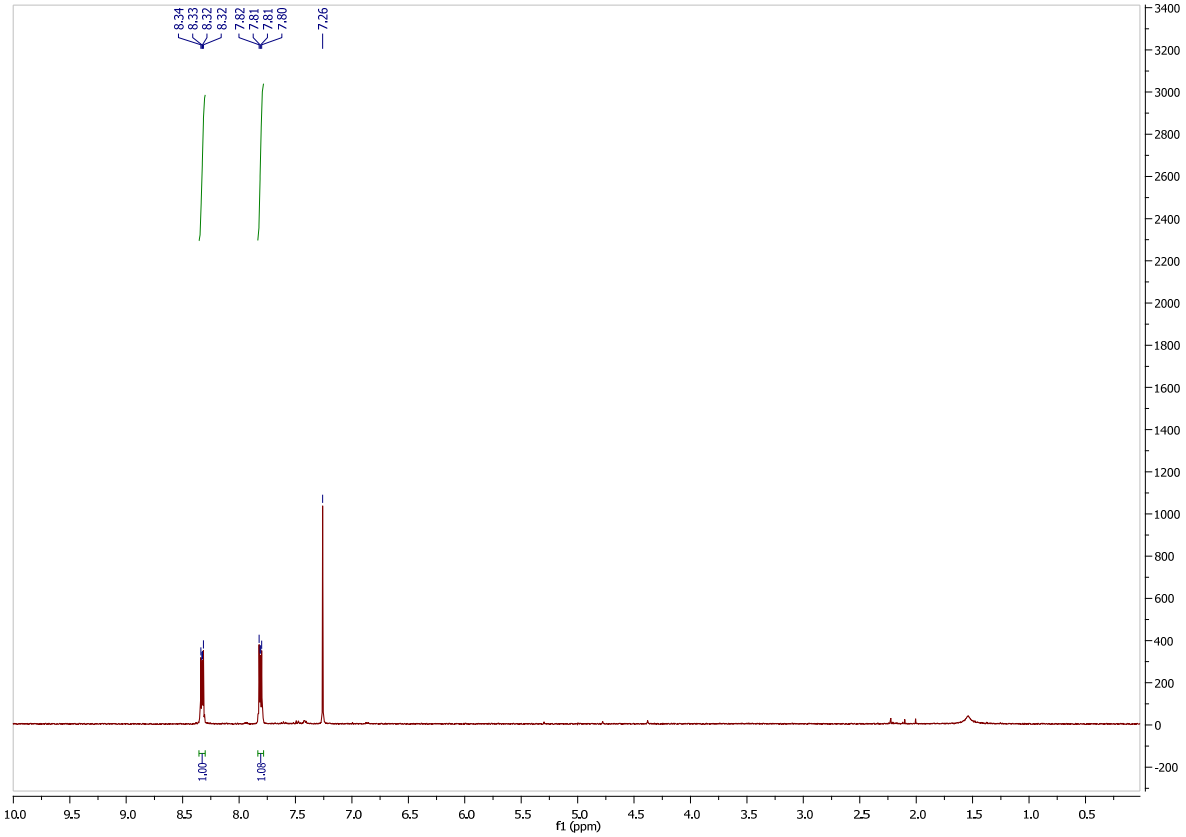


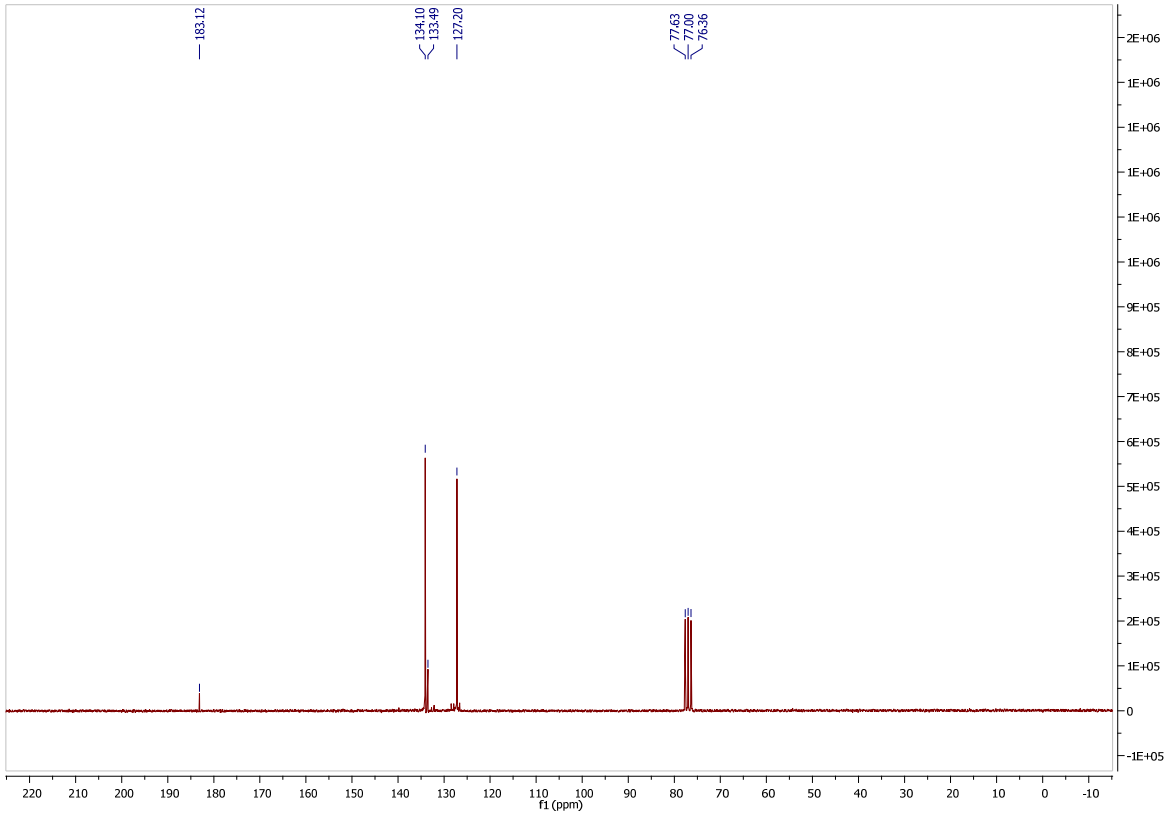

195.93
135.24
134.25
126.71
77.63
77.00
76.36
37.52
f1 (ppm)

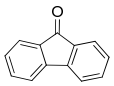


anthracene-9,10-dione (Table 2, entry 7) Isolated directly after workup without purification. The title compound was obtained as an orange solid (99% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.32 (m, 4H), 7.82-7.80 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.1, 134.1, 133.5, 127.2.

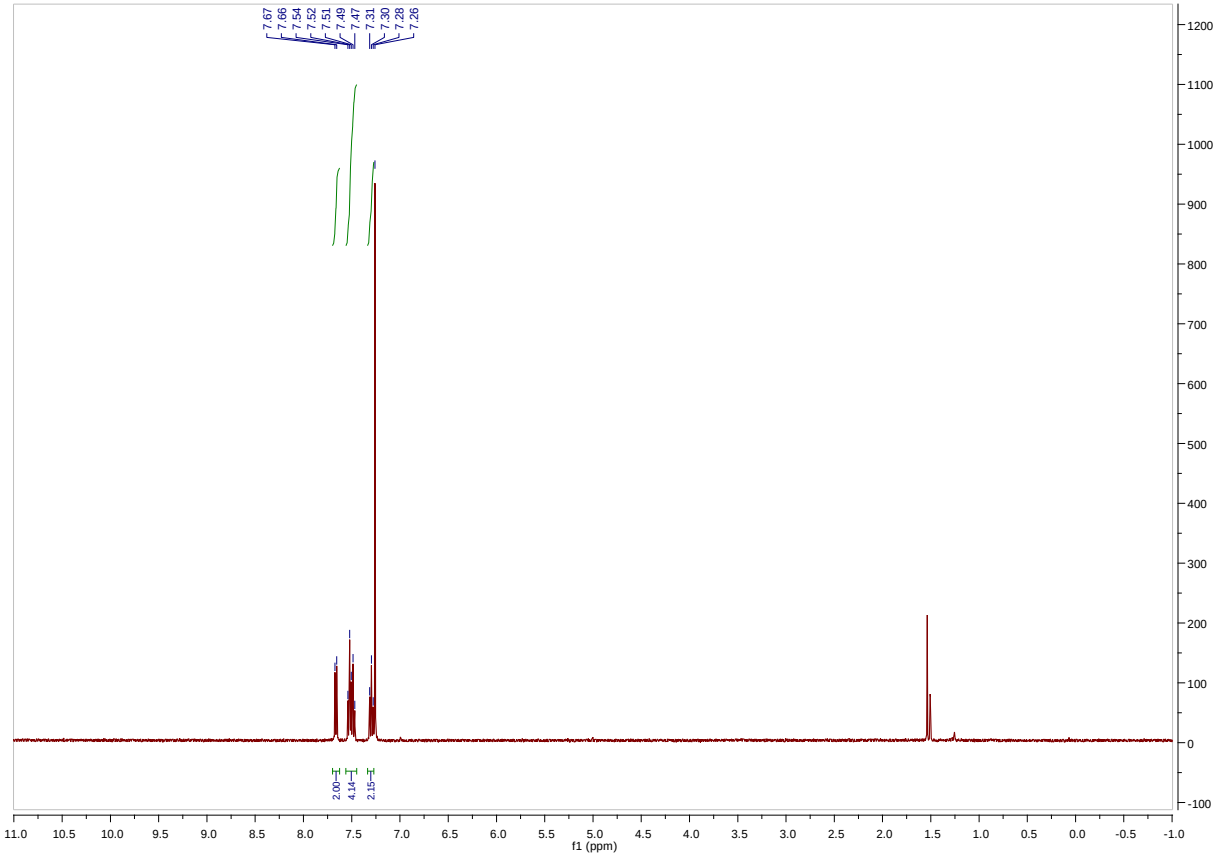


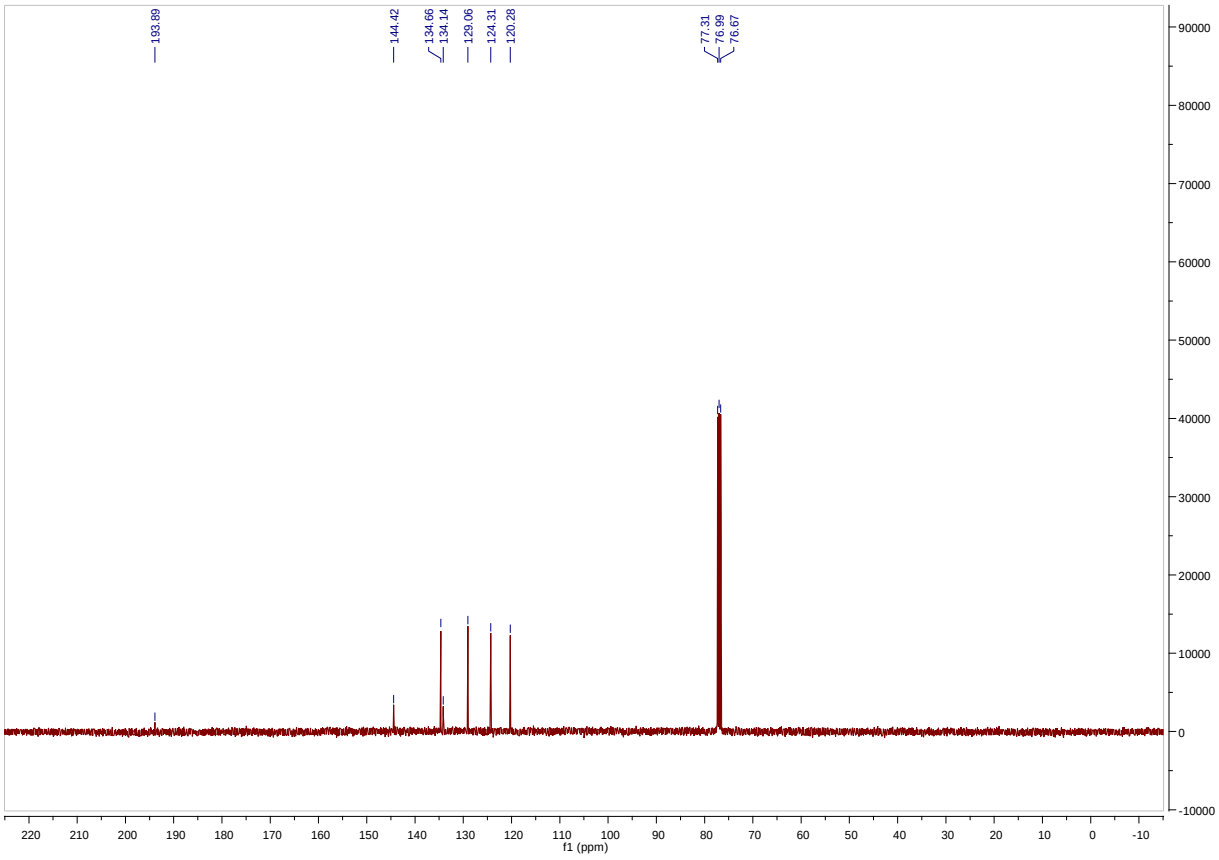

183.12
134.10
133.49
127.20
77.63
77.00
76.36
2E+06
1E+06
1E+06
1E+06
1E+06
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
-1E+05
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

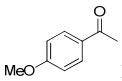


9H-fluoren-9-one (Table 2, entry 8) Isolated by flash column chromatography on silica gel (pentane/ether = 80/20), Rf = 0.5).The title compound was obtained as a yellow oil (76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.66 (m, 2H), 7.54-7.47 (m, 4H), 7.31-7.28 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 144.4, 134.7, 134.1, 129.1, 124.3, 120.3.

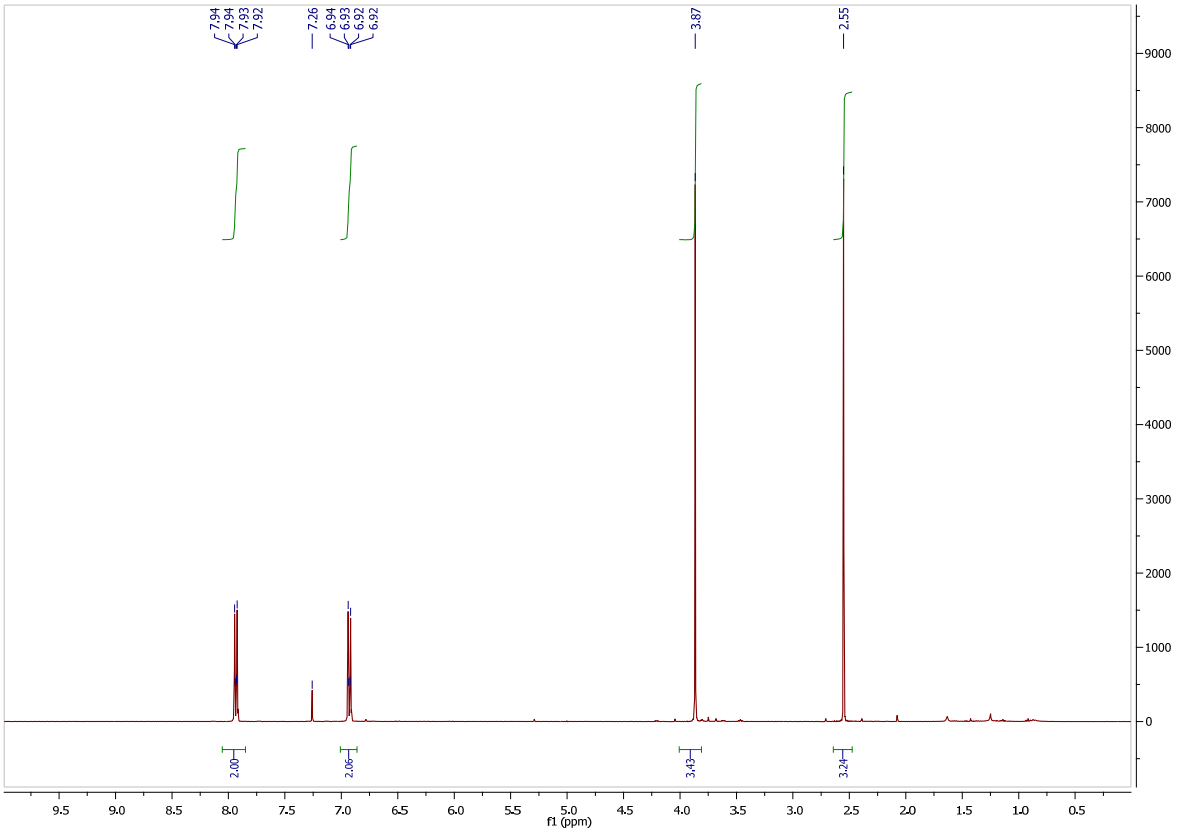


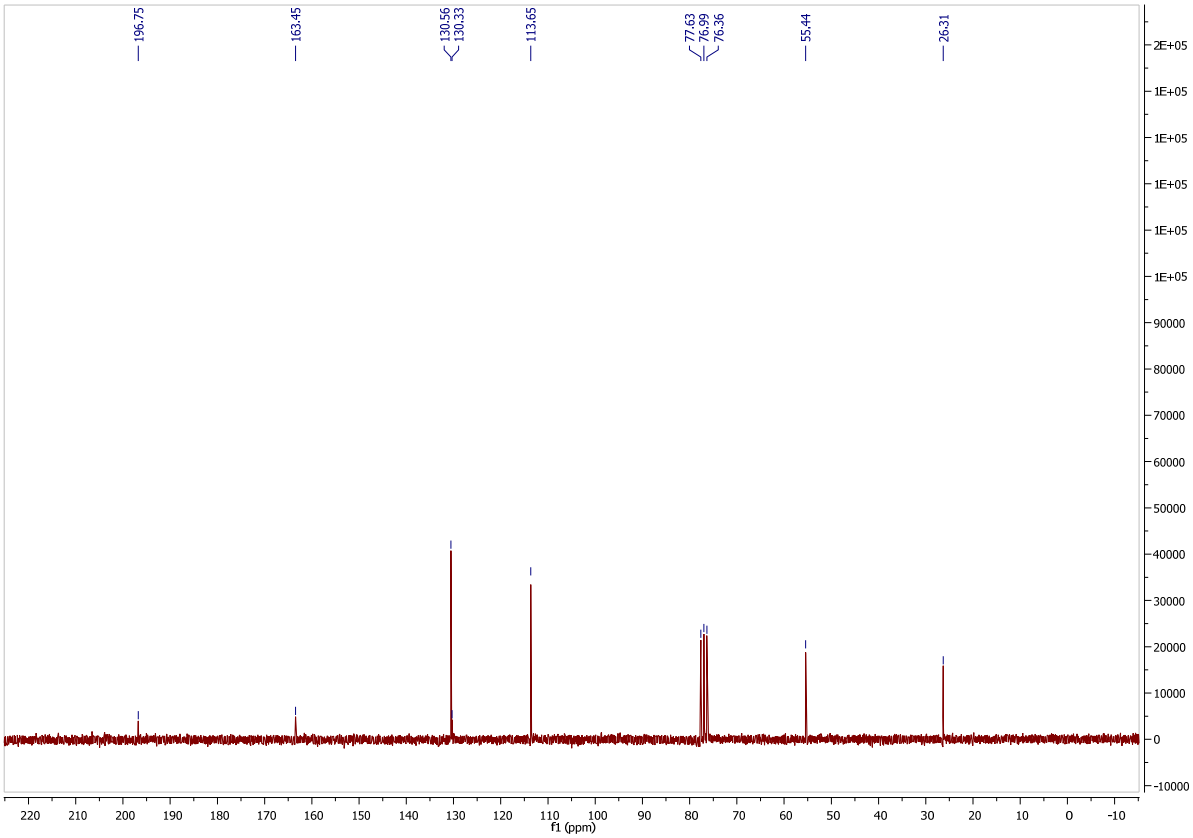

193.89
144.42
134.66
134.14
129.06
124.31
120.28
77.31
76.99
76.67
f1 (ppm)

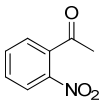


1-(4-Methoxyphenyl)ethanone (Table 2, entry 10) Isolated by flash column chromatography on silica gel (pentane/ether = 8/2, Rf = 0.5).The title compound was obtained as a yellowish oil (28% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.92 (m, 2H), 6.94-6.92 (m, 2H), 3.87 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 163.5, 130.6, 130.3, 113.7, 55.4, 26.3.

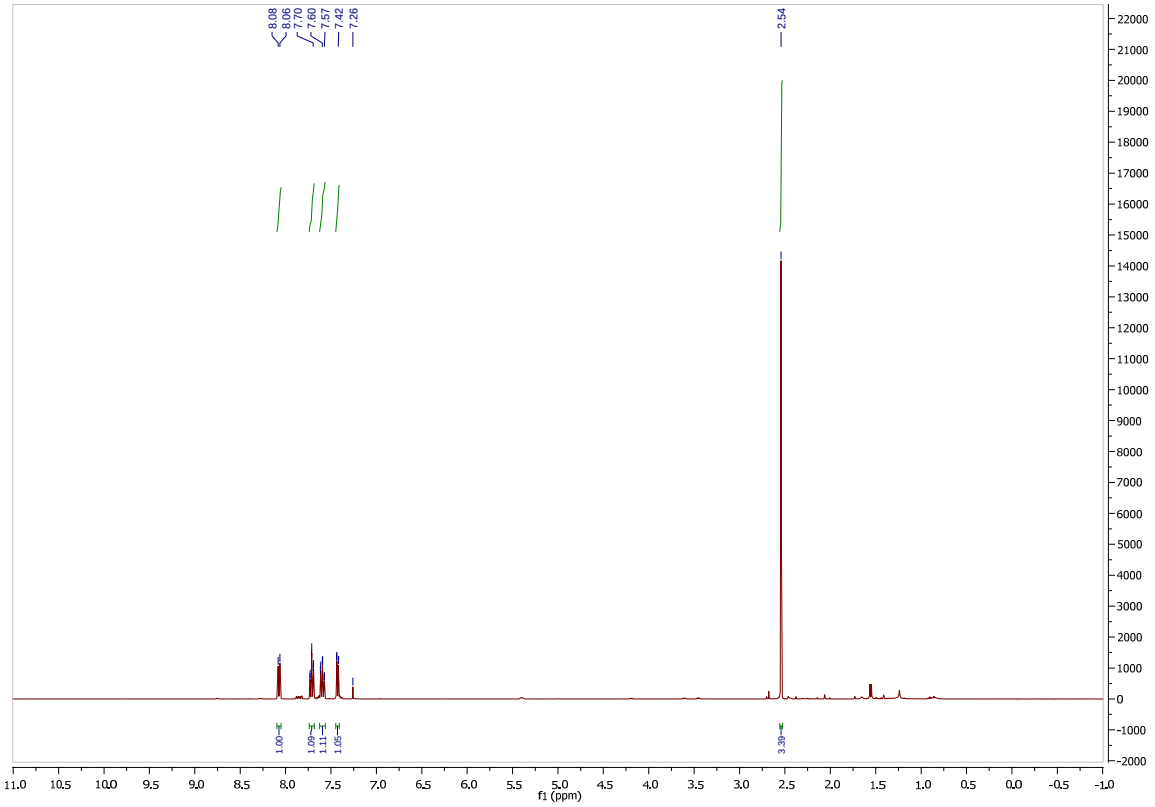


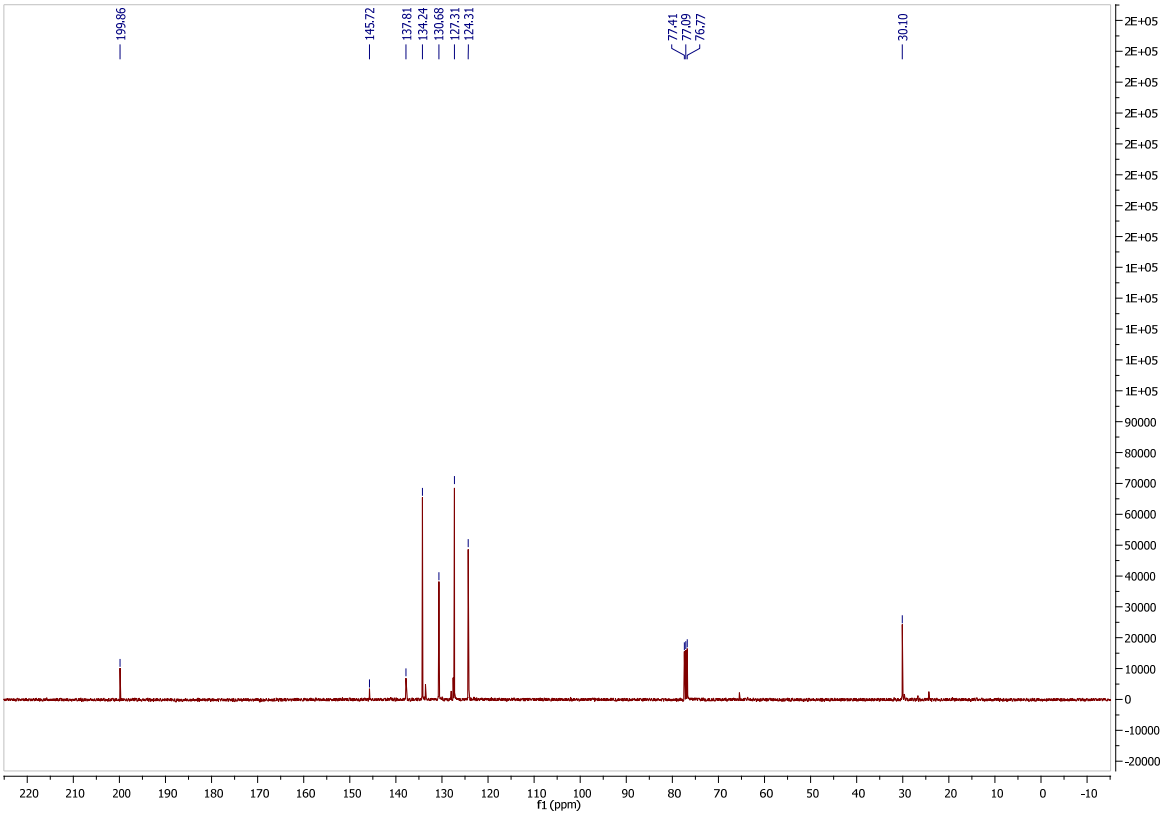

196.75
163.45
130.56
130.33
113.65
77.63
76.99
76.36
55.44
26.31
2E+05
1E+05
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

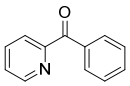


1-(2-nitrophenyl)ethanone (Table 2, entry 11) Isolated by flash column chromatography on silica gel (pentane/ether = 80/20), Rf = 0.5).The title compound was obtained as a colorless oil (17% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 1H), 7.73-7.69 (m, 1H), 7.62-7.57 (m, 1H), 7.44-7.42 (m, 1H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 145.7, 137.8, 134.2, 130.7, 127.3, 124.3, 30.1.

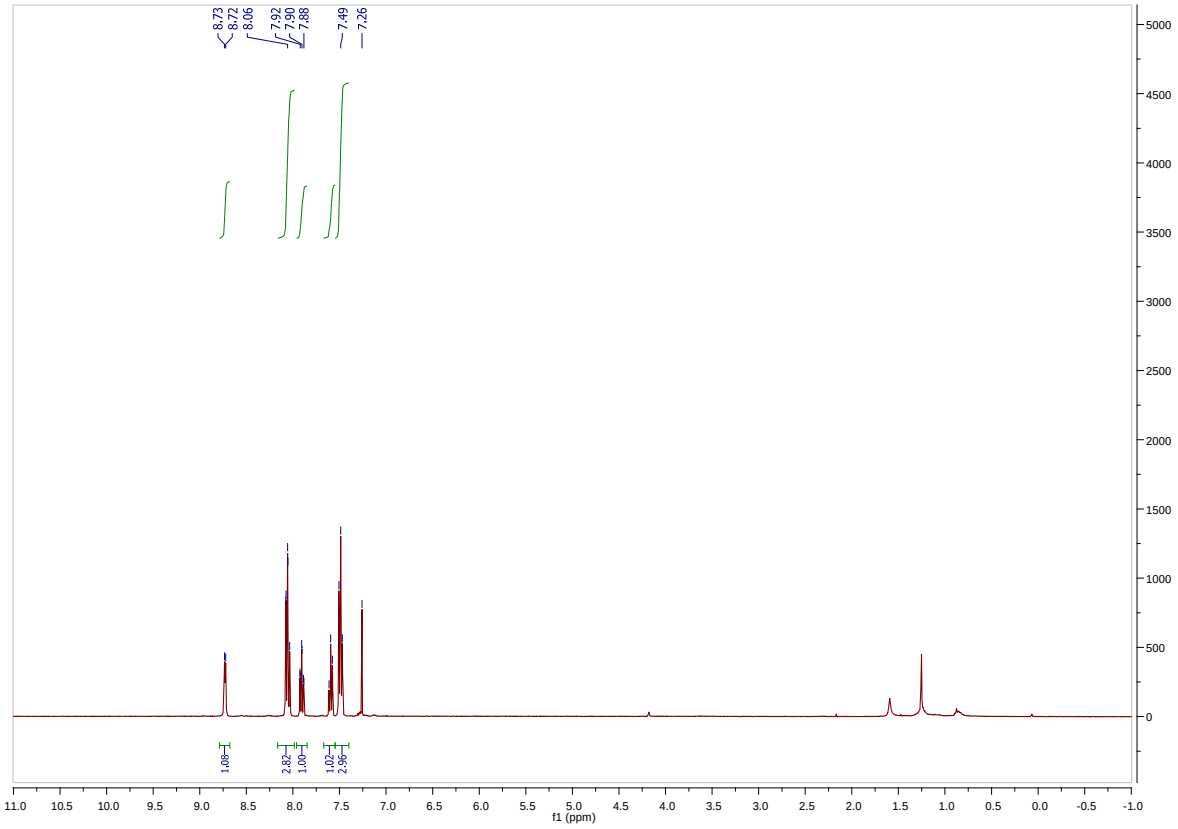


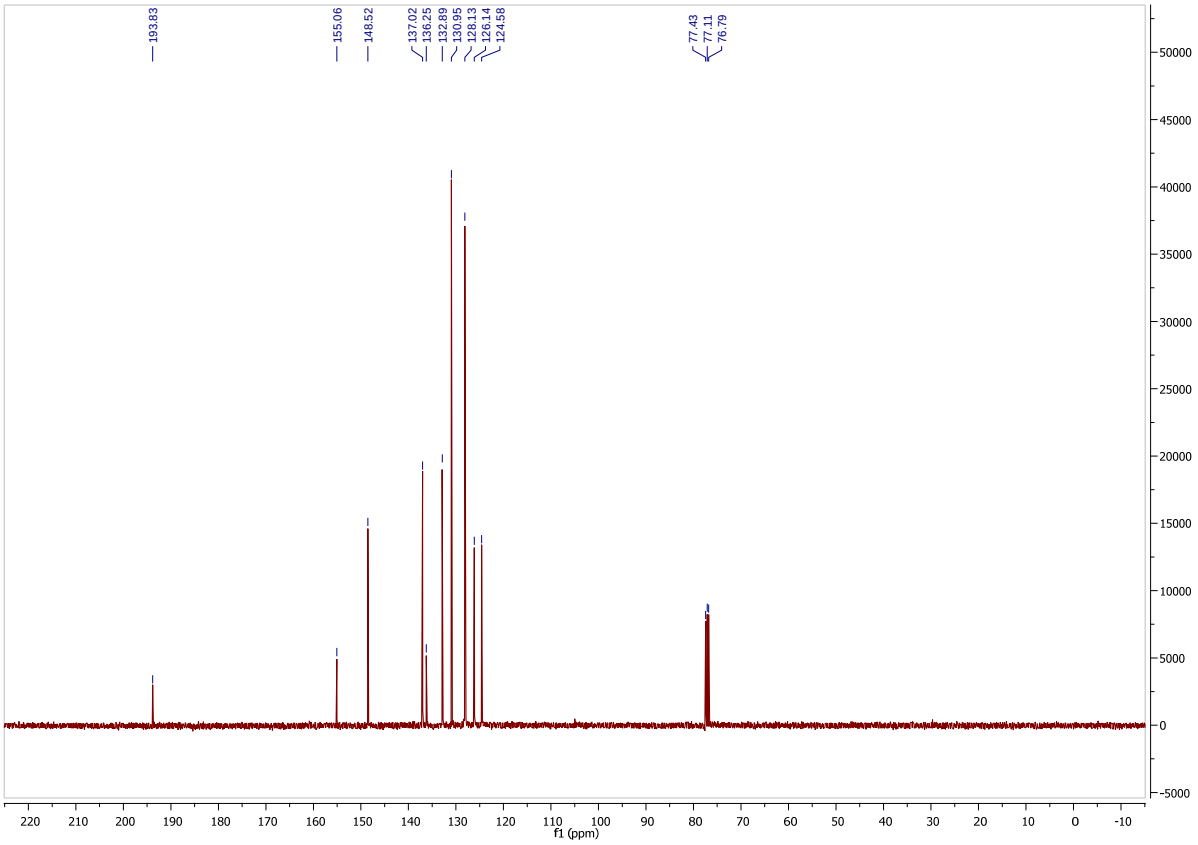

199.86
145.72
137.81
134.24
130.68
127.31
124.31
77.41
77.09
76.77
30.10
f1 (ppm)

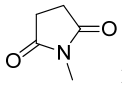


phenyl(pyridin-2-yl)methanone (Table 2, entry 12) Isolated by flash column chromatography on silica gel (pentane/ether = 80/20), Rf = 0.5).The title compound was obtained as a light brown oil (73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.5 Hz, 1H), 8.05 (m, 3H), 7.91 (m, 1H), 7.59 (m, 1H), 7.49 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 155.1, 148.5, 137.0, 136.3, 132.9, 131.0, 128.1, 126.1, 124.6.

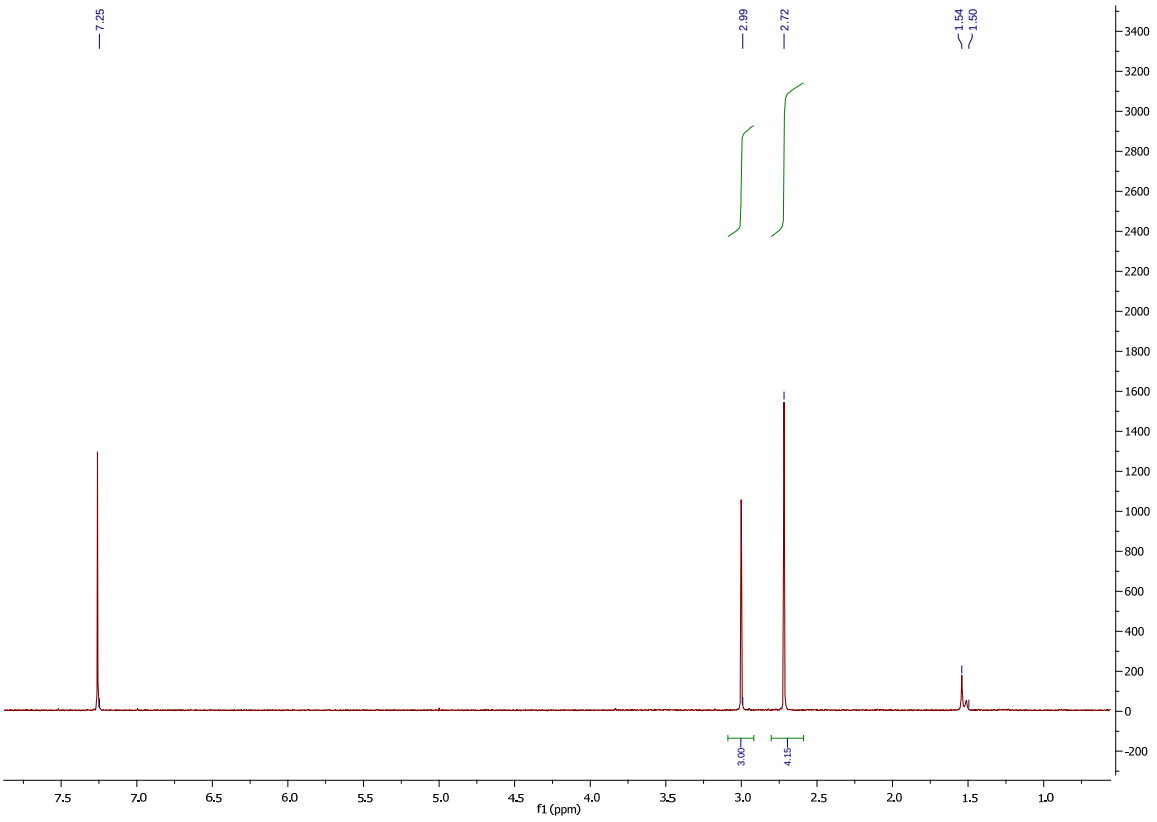


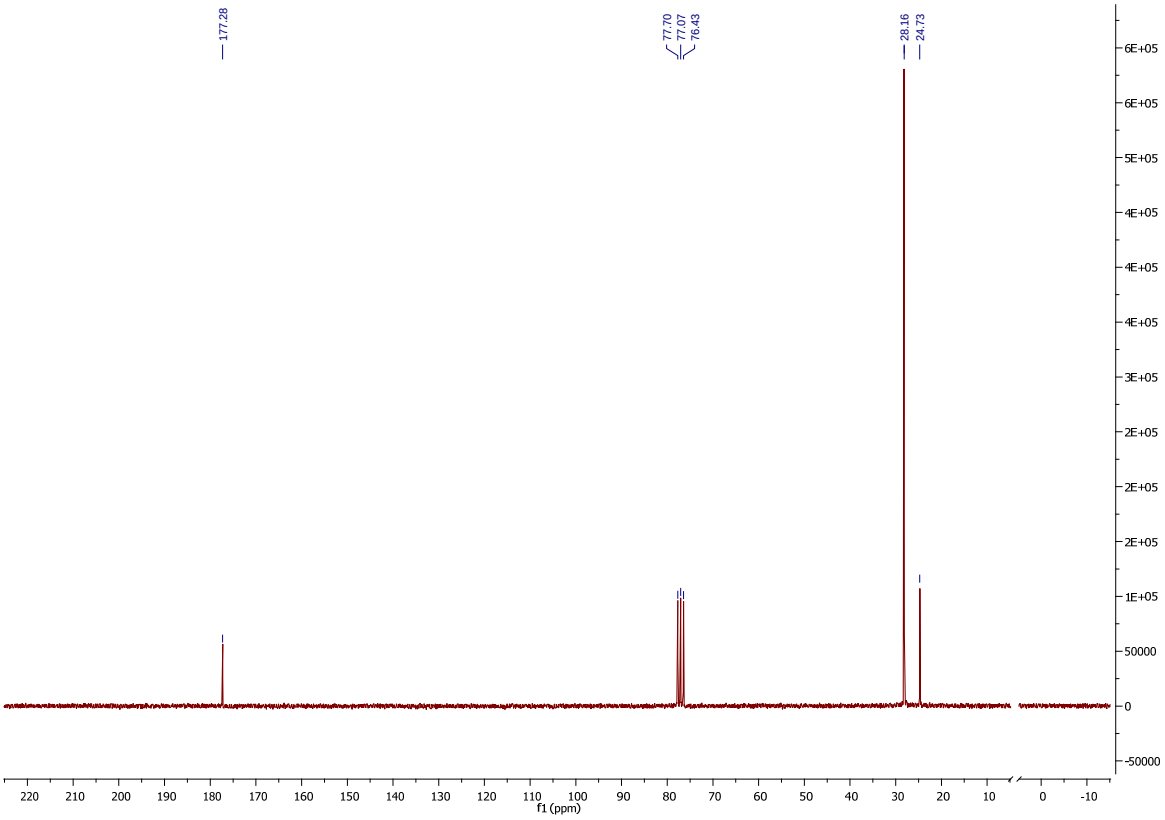

193.83
155.06
148.52
137.02
136.25
132.89
130.95
128.13
126.14
124.58
77.43
77.11
76.79
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



1-methylpyrrolidine-2,5-dione (Table 2, entry 13) Isolated by flash column chromatography on silica gel (pentane/ether = 50/50), Rf = 0.5).The title compound was obtained as a white solid (34% yield).

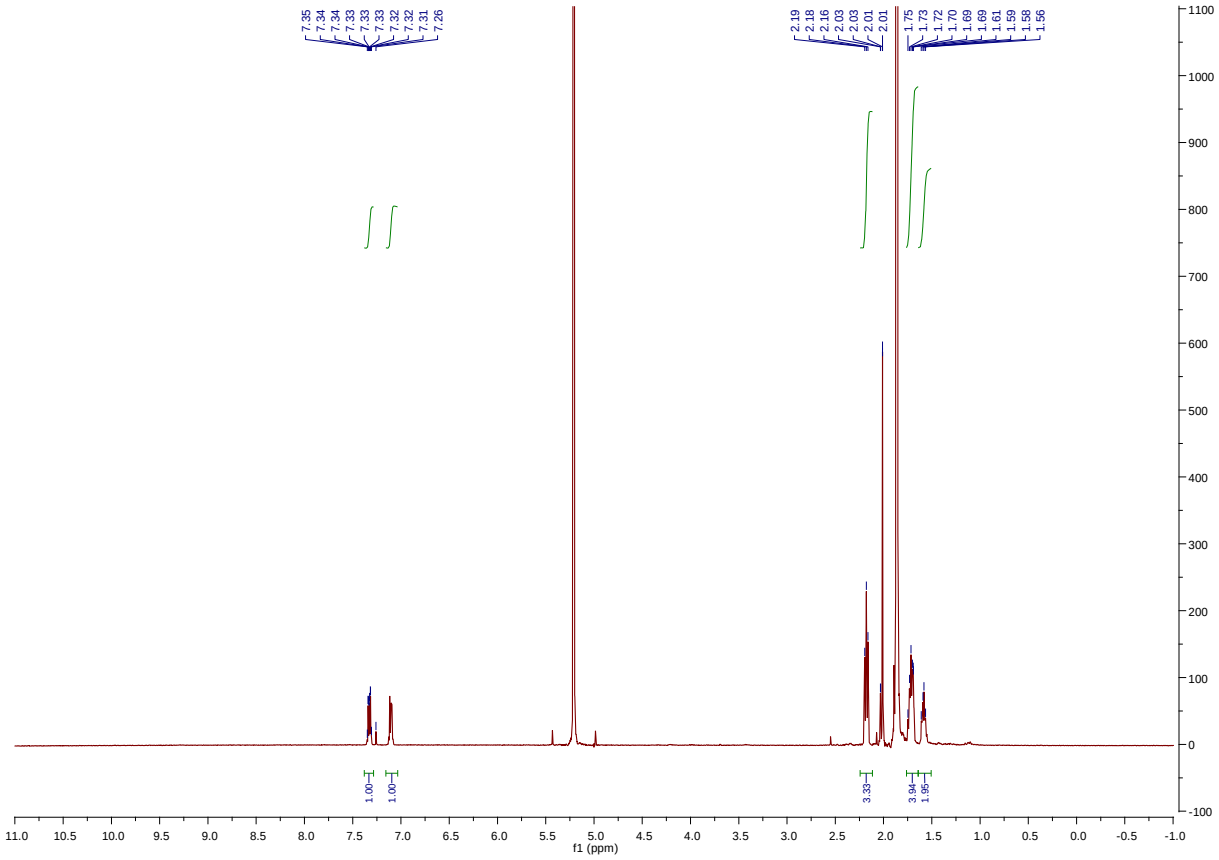
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (s, 3H), 2.72 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 28.2, 24.7.



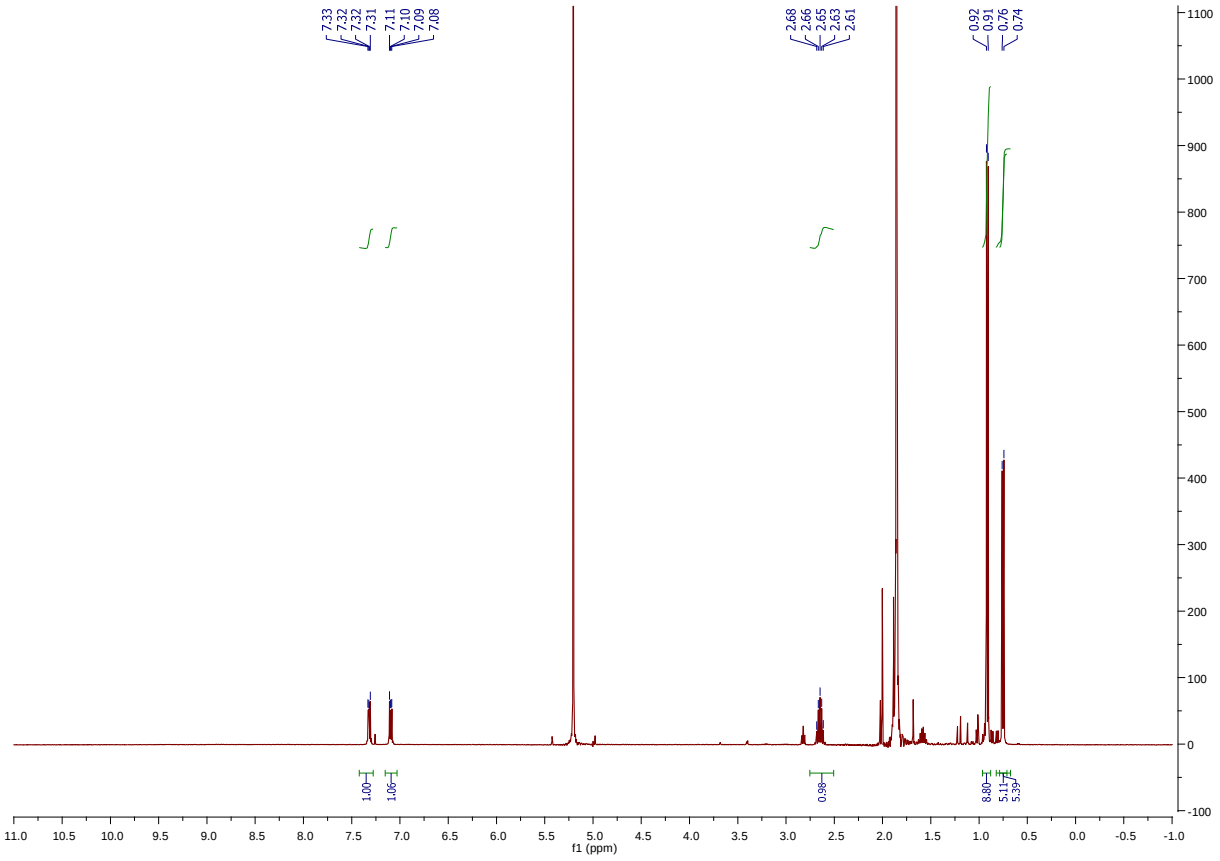

177.28
77.70
77.07
76.43
28.16
24.73
6E+05
6E+05
5E+05
4E+05
4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
50000
0
-50000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4. ^{1}H NMR spectra of crude products

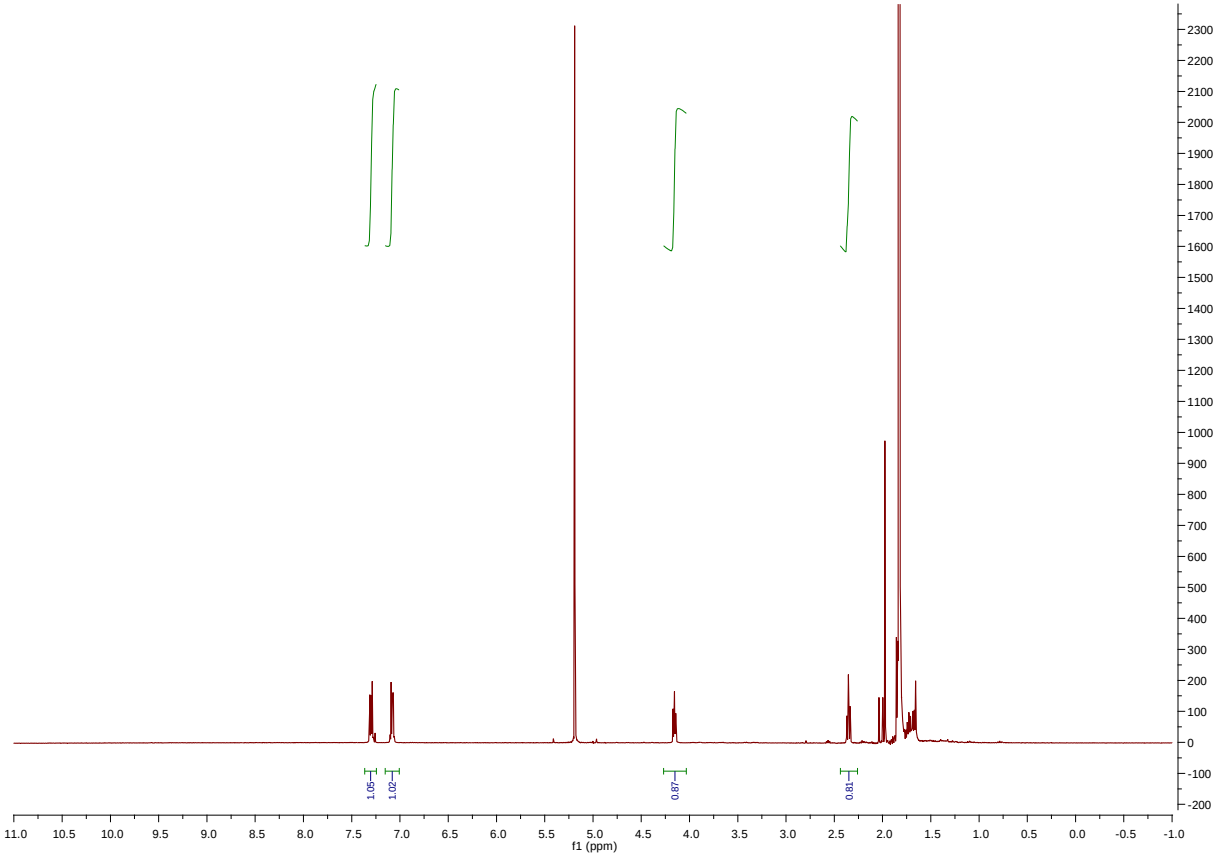
Cyclohexanone (Table 1, entry 1) ^{1}H NMR spectrum in $CDCl_3$ of crude product obtained by extraction with dichloromethane, dichlorobenzene was added prior to extraction as internal standard.

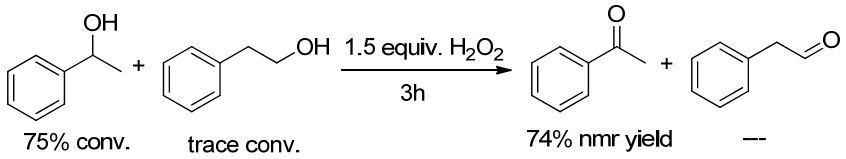


2,4-dimethylpentan-3-one (Table 1, entry 5) ^{1}H NMR spectrum in $CDCl_3$ of crude product obtained by extraction with dichloromethane, dichlorobenzene was added prior to extraction as internal standard.



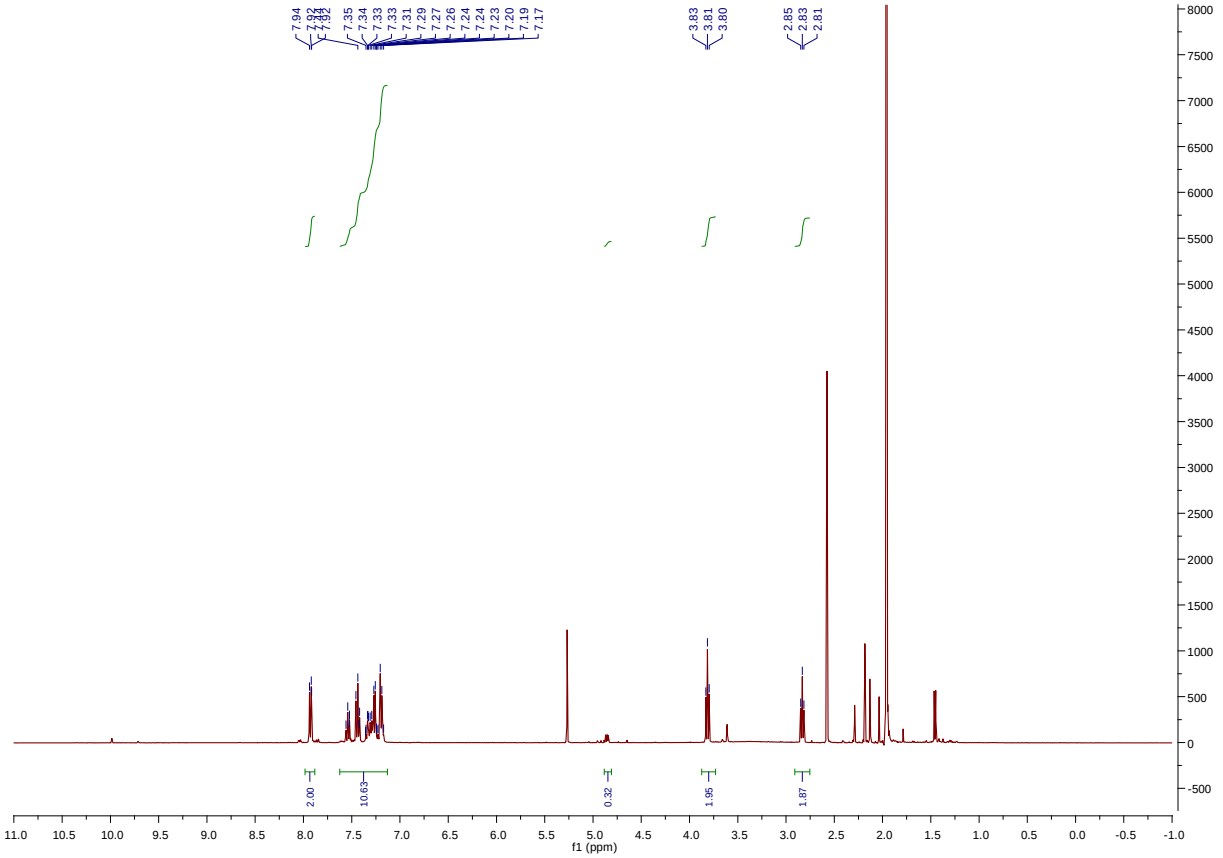
tetrahydro-2H-pyran-2-one (Scheme 3) ^{1}H NMR spectrum in $CDCl_3$ of crude product obtained by extraction with dichloromethane, dichlorobenzene was added prior to extraction as internal standard.



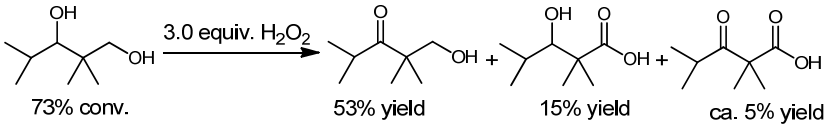


Scheme 4

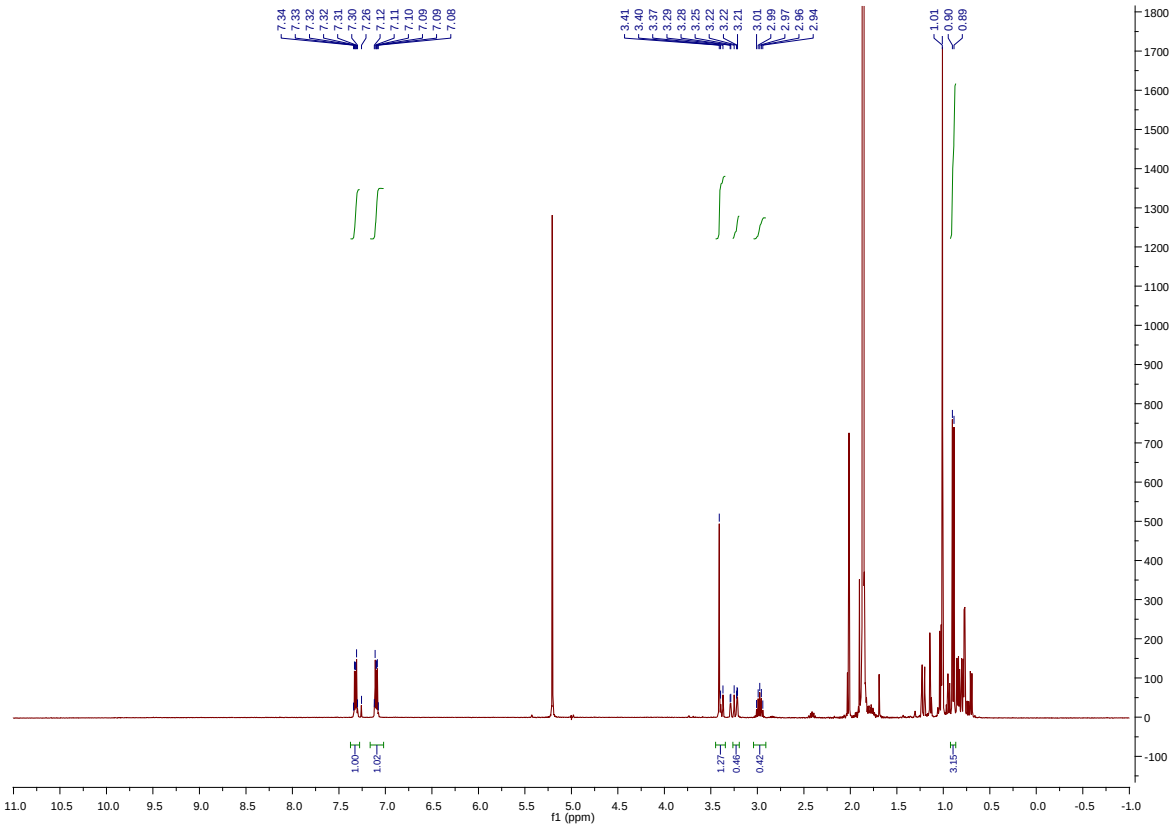
^{1}H NMR spectrum in $CDCl_3$ of crude product obtained by extraction with dichloromethane, dichlorobenzene was added prior to extraction as internal standard.

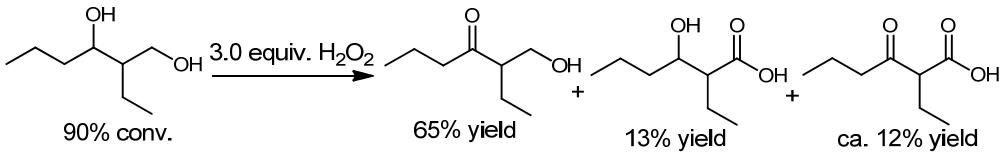


Scheme 5



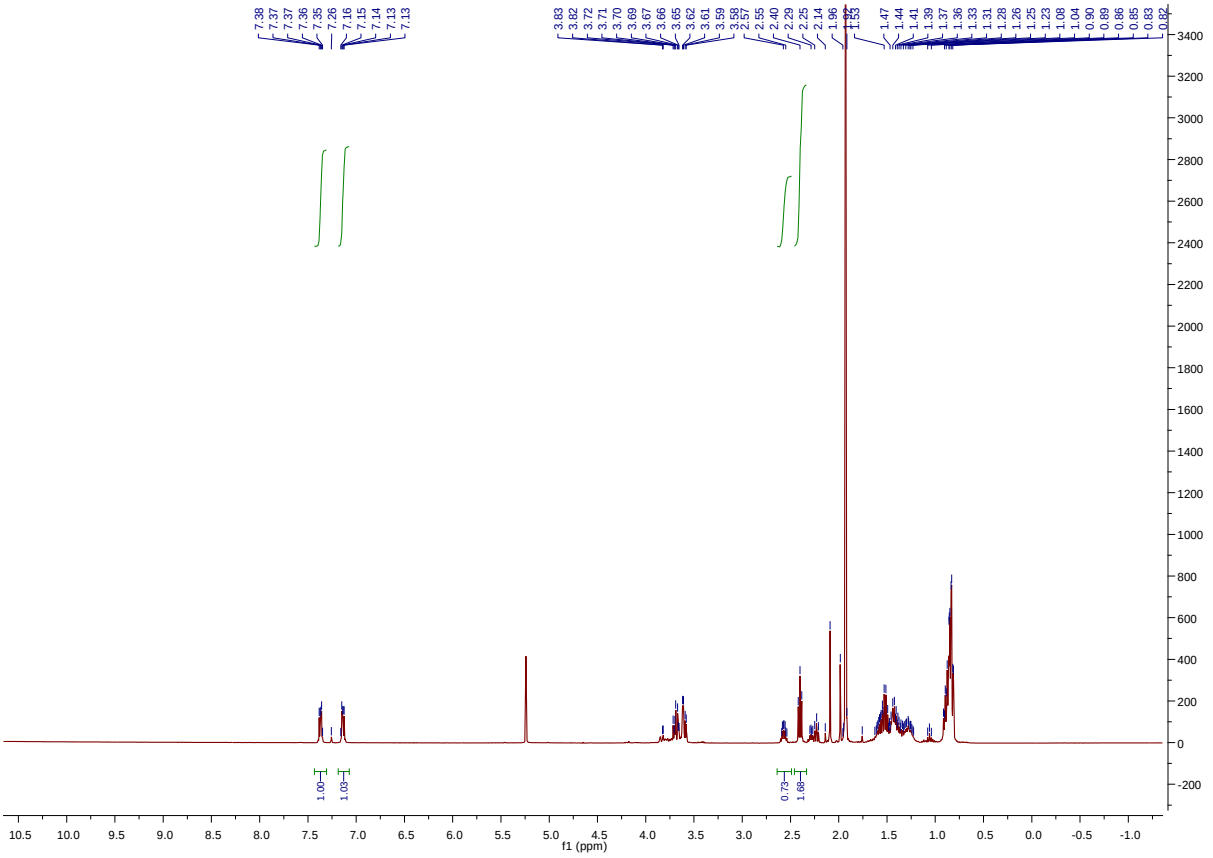
^{1}H NMR spectrum in $CDCl_3$ of crude product obtained by extraction with dichloromethane, dichlorobenzene was added prior to extraction as internal standard.

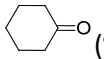




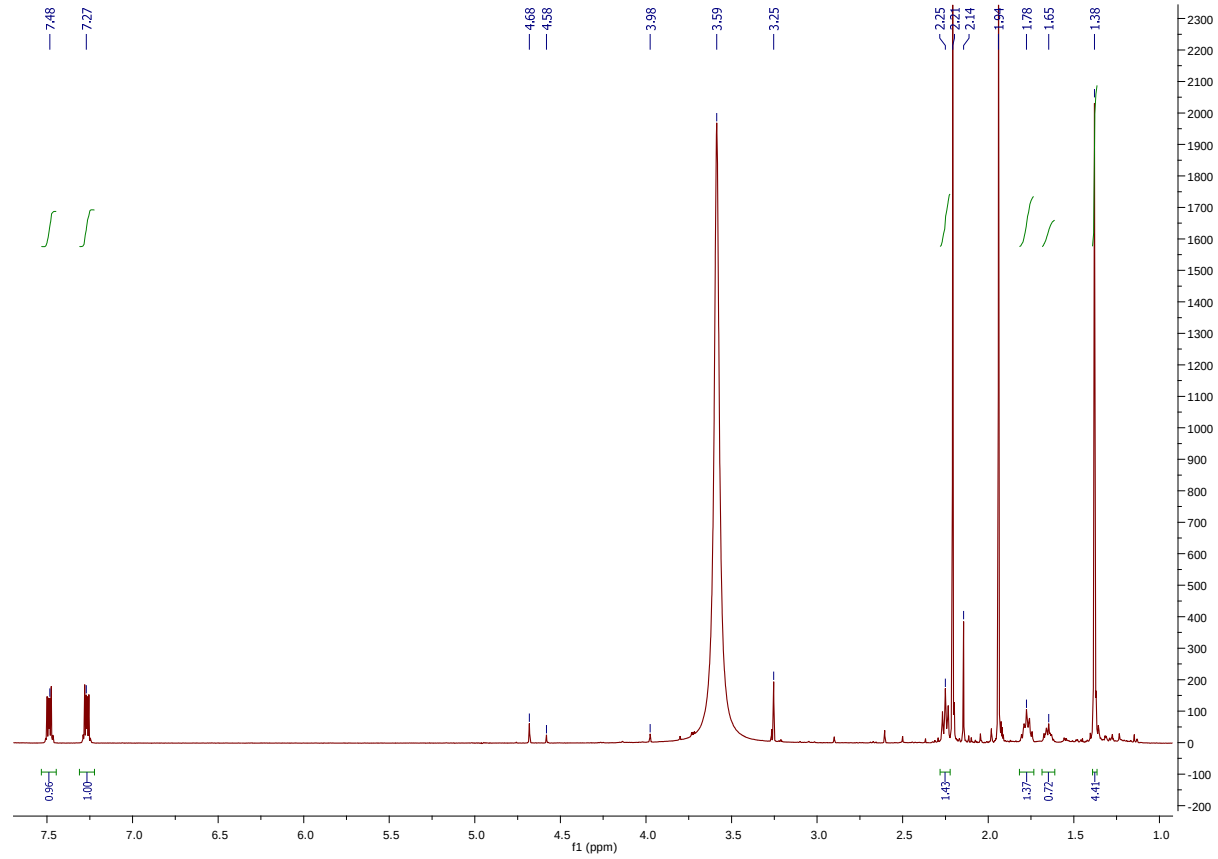
Scheme 5

^{1}H NMR spectrum in $CDCl_3$ of crude product obtained by extraction with dichloromethane, dichlorobenzene was added prior to extraction as internal standard.

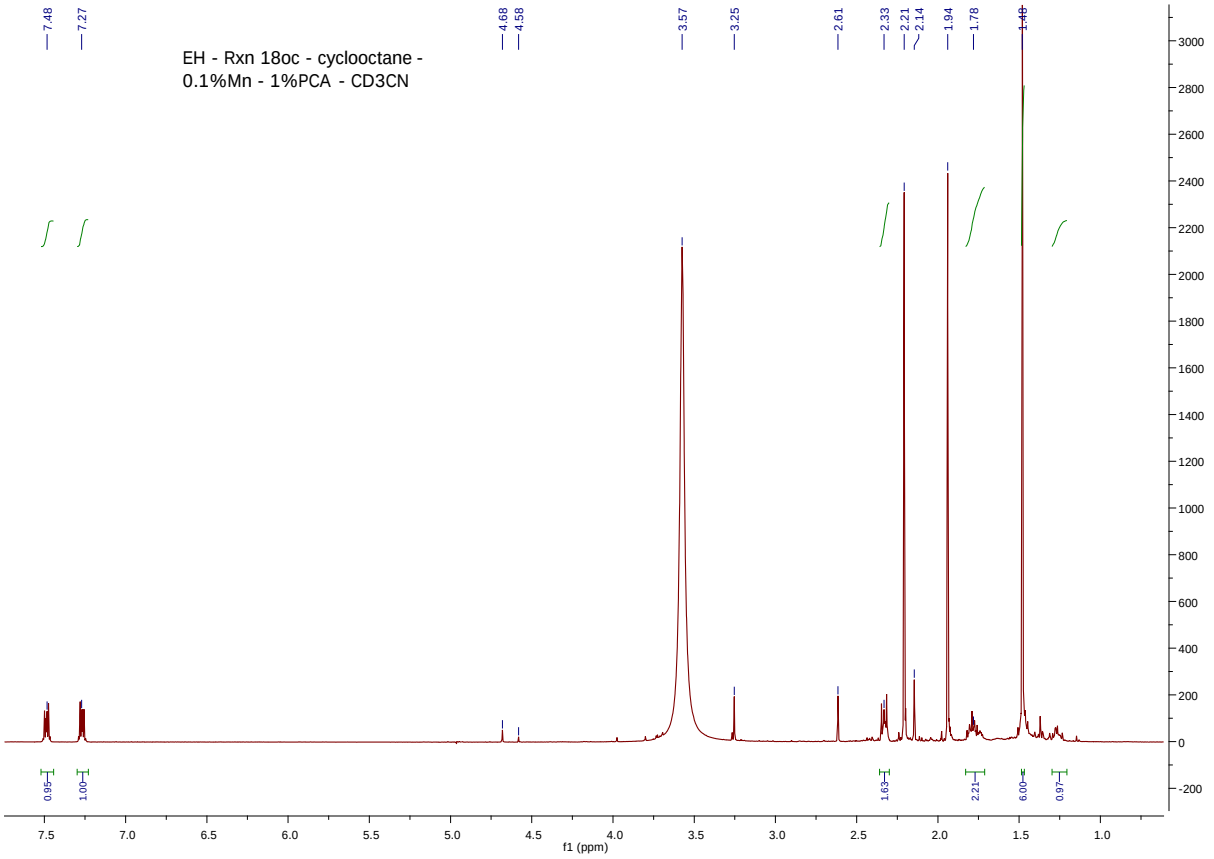


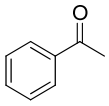


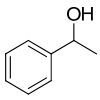
(Table 2, entry 1) ^{1}H NMR spectrum in CD_3CN. The reaction was performed in CD_3CN, tetrachloroethane was added as internal standard.



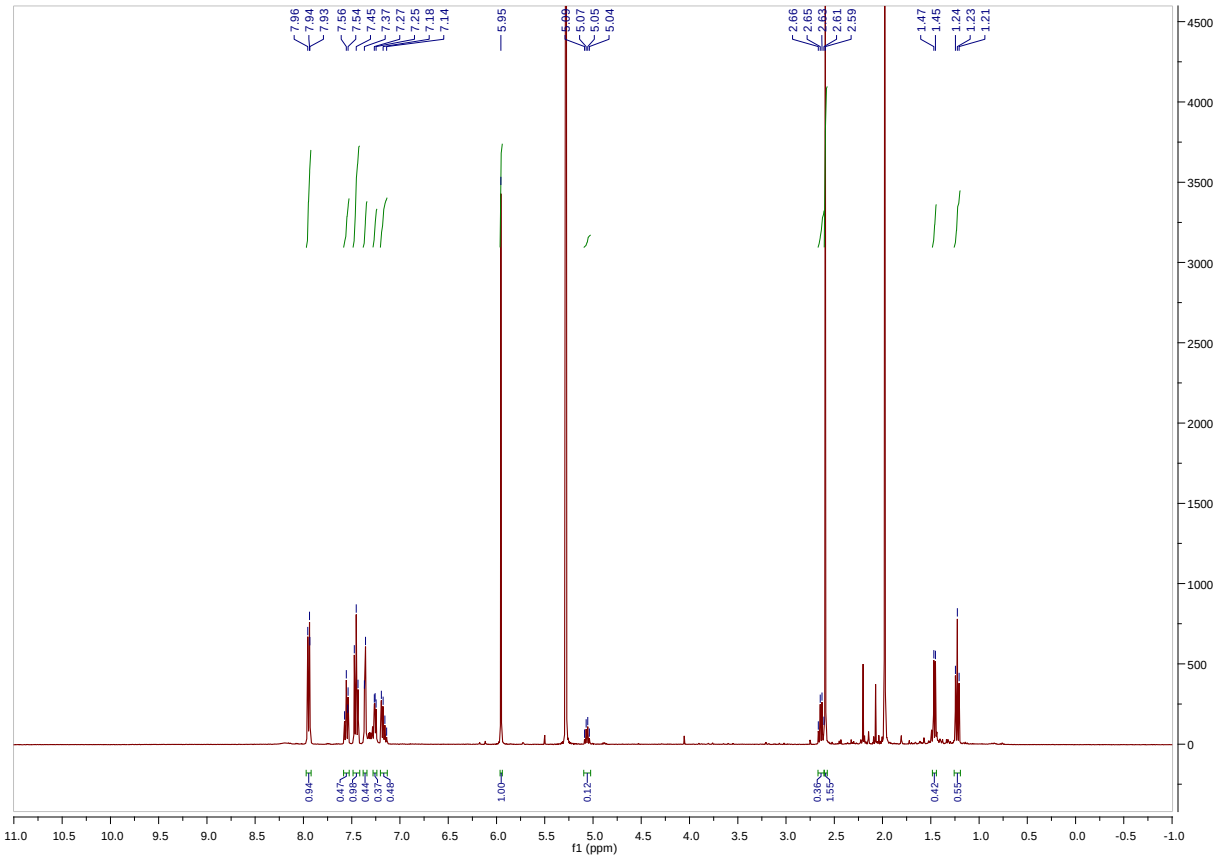
(Table 2, entry 2) ^{1}H NMR spectrum in CD_3CN. The reaction was performed in CD_3CN, tetrachloroethane was added as internal standard.

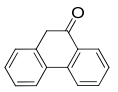


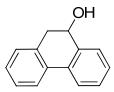


and


(Table 2, entry 3) ^{1}H NMR spectrum in $CDCl_3$ of crude product obtained by extraction with dichloromethane. Tetrachlorethane was added as internal standard.





and


(Table 2, entry 9) ^{1}H NMR spectrum in $CDCl_3$. Tetrachloroethane was used as internal standard and added to reaction mixture prior to dilution in $CDCl_3$.